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OF THE

ASME/EPA HAZARDOUS WASTE INCINERATION CONFERENCE

MAY 27-29, 1981
WILLIAMSBURG, VA

Cosponsored by:

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Solid Waste Processing Division

EPA United States Environmental Protection Agency
Industrial Environmental Research Laboratory-Cincinnati

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INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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Donald A. Oberacker, EPA/IERL-Ci
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This report is a proceedings of a 3-day conference among industry, government, professional engineers and scientists, and the general public concerning hazardous waste incineration which came at a time when EPA interim final rule incineration regulations had just been made public. A number of topical papers were presented which represent a cross section of a part of the incineration technology in use and under regulatory examination during this period. The proceedings cover a conference which was co-supported by EPA and the American Society of Mechanical Engineers which was organized as a cooperative agreement grant effort from the EPA in the spirit of professional interest and public discussion of the thermal disposal technologies and their regulation.

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This is a proceedings of an ASME/EPA conference held with the purpose of serving as a public forum and to promote informal information exchange on the new and developing field of hazardous waste incineration technology. The proceedings are published in an unpeer-reviewed and as-received-from-the-speaker format, having not been subjected to the normal EPA internal technical or Administrative review procedures in the interest of releasing the information as presented by a number of speakers representing a variety of government and industrial backgrounds. Additionally, this waiver of normal review and format procedures occurred during the Agency's temporary period of publishing budget curtailments during the 1981-1982 period.

FOREWORD

Over 300 persons attended the ASME/EPA Hazardous Waste Incineration Conference held in Williamsburg, Virginia, May 27, 1981. Twenty timely papers were presented in four sessions. Conference plans called for publication of these papers by EPA shortly after the Conference. Fiscal restraints have prohibited the EPA from publishing the Conference Proceedings.

Believing that the papers merit publication, the ASME Solid Waste Processing Division elected to reproduce abstracts for all of the papers presented and reproduce the 14 papers that have been submitted for publication. The papers submitted have been reproduced as submitted and have not been subject to the normal ASME peer review. Thus, these Proceedings are a reproduction service for those who attended the Conference.

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OPENING REMARKS

PUBLIC HEALTH CONCERNS AND THE INCINERATION OF HAZARDOUS WASTES

C. O. VELZY
Charles R Velzy Associates, Inc.
Armonk, NY

Introduction

On Monday night, May 12, 1980, at the ASME Solid Waste Processing Division's Biennial Conference in Washington, DC, two separate meetings were held involving Division and EPA personnel. In the first meeting, preliminary plans for this Hazardous Waste Incineration Conference were discussed. At the second, later, meeting results of recent tests on a resource recovery plant were presented and discussed. During these tests Dioxin had been found on particulates extracted from the plant's stack. News of this finding leaked to the public press created great public concern and this fact, along with other problems faced by the plant, resulted in the plant being closed. It was pointed out that this discovery boded no good for the developing energy-from-waste field. It certainly was not good news considering the current increasing interest, in both private and government sectors, in the incineration of hazardous wastes.

In considering the impact of public health concerns on the suitability of, and the ability to implement, projects involving incineration of wastes, several factors must be evaluated. First, are the reports of investigators having found Dioxin and other trace toxic emissions correct and, if so, what are the implications? How should such information be treated in the public press (and how is it likely to be treated)? How can the risks posed by such discharges best be assessed, and allowable emission levels for these substances be established? Is zero risk or zero discharge realistic? I will attempt to address these issues herein.

Dioxins and Other Trace Emissions

As a result of the concerns generated at the meetings held on May 12, 1980, the ASME Research Committee on Industrial and Municipal Waste commissioned a study and report on state-of-the-art of detection, quantification, toxicology, and potential generation and discharge of trace organic emissions from combustion processes, with particular emphasis on 2,3,7,8 tetrachloro dibenzo-para-dioxin (2,3,7,8-TCDD). The document, including a basic report prepared by A.D. Little, Inc. (ADL), discussion comments by over two dozen peer reviewers, and rebuttal to the comments by ADL, was completed in January of 1981 and released for distribution this past April.

The technical findings related to detection and quantification may be summarized by noting that methods currently exist to analyze for Dioxin and other toxic substances in trace concentrations as low as parts per billion and lower. Sampling and extraction procedures, however, are not ideal and are the subject of substantial discussion in the technical community. The implication of the above is that, while over the past several years we have developed the capability to detect the presence of minute quantities of toxic substances, we are not too sure about the absolute quantity or the rate of discharge.

With respect to toxicology, substantial literature has been published on this subject, particularly with respect to 2,3,7,8-TCDD, over the past several years. Much of the information is related to dosage tests on small animals. The results of these tests indicates that 2,3,7,8-TCDD is one of the most toxic substances known to man. Other isomers of the polychlorinated dibenzo-para-dioxins (PCDD) are only slightly toxic. However, in spite of the extreme toxicity of 2,3,7,8-TCDD, in the several instances where accidental or occupational exposure has occurred, no deaths of humans have been confirmed. Of course, as indicated above, it is very difficult in these instances to determine the actual exposure levels at the time and place of exposure.

Determination of the potential generation, emission and control of Dioxins from combustion processes is very difficult and controversial. Currently there are two basic theories proposed to explain the presence of Dioxin on fly ash from combustion processes. One theory holds that precursors (chlorinated organic compounds, chlorinated plastics, etc.) must be present in the input to the combustion process. A second theory is that any hydrocarbon material combusted in the presence of chlorine will produce trace amounts of PCDD, along with trace amounts of numerous other chemicals, during the combustion process. Since the sophisticated instruments and the required methodology to detect trace amounts of chemicals has only become available within the past several years, little or no definitive information exists with respect to chemicals produced in trace amounts (parts per billion or lower) during the combustion process. If the first theory is correct, the toxic chemicals could be controlled or eliminated by control or elimination of the precursors. If the second theory is correct, control or elimination of toxic chemicals could best be accomplished by "properly" controlling the combustion process.

Thus, from the above, I think we may conclude that we presently have the analytical capability to test for and demonstrate the presence of trace toxic chemicals in many substances including emissions from the combustion process. However, we do not have adequate techniques available to sample and quantify these substances. This problem, along with the very great cost of regional health studies, makes it very difficult to develop proper emission control strategies or conduct cost benefit analyses of different control strategies.

Treatment of Emissions of Toxics in the Press

One can expect the finding of toxic chemicals in the environment to be closely covered by the public press in the near future. Starting with Love Canal, the media, more and more, has been focusing on the very real problem of hazardous waste disposal. Too often, the reporting plays solely on the increasing public fear of hazardous or toxic materials with little or no attempt to place the problem in perspective. Thus, within two weeks, earlier this year, the following three articles appeared in New York newspapers or national magazines: "Study Links Dioxin with Rare Cancer"; "Dioxin Haunts EPA Refuse Plans"; and, "More Toxins Found by State at its Binghamton Building".

Of course, properly assessing the risk to public health posed by toxic materials in trace concentrations in the environment is not a simple matter. The general approach entails following detailed procedures to concentrate the toxic material and feeding it to rats or other mammals with a short life span. The development of tumors, birth defects or reproductive disturbances are compared to control groups and the results extrapolated to human populations exposed at low concentrations. The continued improvement in monitoring and analytical technology will permit the detection of ever smaller concentrations of organic residuals and other trace toxic materials. Therefore, more and more in the future the presence of toxic material will be determined while there is little or no understanding of the degree of risk represented by the concentration at which it is found.

Recognizing the difficulty in addressing this problem, the technical community should get its act together and discuss the problem in clear, concise, realistic terms. An example of what not to do appeared in a recent technical journal. The authors spoke of setting emission standards in terms of gathering "data to determine the level at which emissions must be controlled to adequately protect the public", as if this was an absolute threshold value above which the public was endangered, and below which it was safe. Zero risk was discussed as if it were achievable, raising false expectations on the part of someone reading the article. Hazardous waste and "normal municipal waste" was discussed interchangeably in the context of siting problems, creating the potential problem in the eyes of the lay reader that at least these agency personnel looked at "normal municipal waste" as hazardous. It was pointed out that at one of the two plants tested they did not find 2,3,7,8-TCDD, but they neglected to point out that they didn't test for this chemical at that site. Perhaps the entire approach to this article, as a "we" (regulatory agency) - "they" (scientific community) situation, is best summarized by the following quote: "the regulatory agencies were severly hampered in their actions because the scientific experts could not agree on the potential dangers posed by the emissions." I think it is a mistake to attempt to lay the "blame" for our inability to act promptly and decisively in the area of trace toxic contaminants in administering fixed numerical emission standards on a go/no-go basis at the feet of the "other guys", the scientific community. Rather we should be using the press to educate the public as to the real nature of the problem with trace toxic emissions, the fact that we do not currently have all the answers, and the fact that there is a risk in producing and handling hazardous materials, as there is in the conduct of our everyday lives.

Risk Assessment

In the reports announcing the discovery of PCDD in the fly ash collected from resource recovery plants, it was generally presupposed that the mere existence of this material constituted a public health problem. In an attempt to provide some focus to this issue and its potential public health significance, the ASME Research Committee, in the Foreword to its Report, compared the apparent risks from stack effluents at existing energy-from-waste plants and other common risks faced by the general public. The risk of contracting cancer due to exposure to TCDD from energy-from-waste plants is projected in this Report on a worst case basis almost to the point of ridculousness. In addition to the implied continuous exposure over one's lifetime to the indicated concentration, an impracticality, and equal absorption through the lungs as through the gastrointestinal tract (considering the liver as the primary organ at risk), an improbability, it is assumed that 100% of the TCDD taken into the lungs is absorbed into the body, another impracticality. Even given these prejudicial assumptions, the risk, based on similar extrapolations for TCDD in water by the NYS Health Department, indicates the potential of one additional cancer case in a population of 1,000,000. This is compared in the Report to involuntary risks such as 200 deaths per million population per year from influenza and 100 deaths per million population per year in the home.

Acceptance of the concept of risk assessment implies that one must first accept the impossibility of zero risk, and that one can then establish an "acceptable" level of risk. As pointed out in the Report, "Zero, in the sense of quantification of trace chemical contaminants, is a moving target with rapid development of analytical instruments having the capability to measure smaller and smaller amounts of chemicals". Establishing an "acceptable" level of risk is at best a very difficult philosophical exercise. Studies of risk benefit controversies have identified many considerations that go into making such decisions. Thus, people are willing to accept much higher self-imposed risks than involuntary risks. Furthermore, the public is much more likely to depend on intuitive interpretations of both risks and benefits than on quantitative estimates from "experts". Generally, the possibility of death from natural hazards of about one per year per million people is considered a negligible risk. However, if you are talking to the particular population segment "at-risk", they may not accept this judgement.

Of course, even if the need to establish an acceptable level of risk to secure the maximum benefit for the largest segment of the population is accepted, this does not preclude the need to conduct investigative programs to better define the problem and to determine potential cost-effective methods for further reducing possible risks to the practicable minimum.

The need to establish fixed, specific regulatory limits is another problem. The regulators and the courts are looking for a "yes" or "no" answer rather than a statistically phrased "maybe". In the matter of trace chemical contaminants, a greater responsibility is placed on the shoulders of the chemists and the regulators, together, to agree upon regulatory limits that clearly fall above the upper limit of the region of uncertain reaction as measured under field conditions by multiple laboratories. These judgements should be made by an expert "disinterested third party" acceptable to the involved adversary groups. Such a third party could be a scientific society such as the American Chemical Society.

Conclusions

Recent studies conducted with currently available state-of-the-art analytical instruments and methodology indicate the probable presence of Dioxins in discharges from combustion processes. Due to the wide variation in toxicities of specific Dioxin isomers, this probability does not automatically indicate the existence of a public health problem. A comparison between risks posed by current reports of concentrations of TCDD in resource recovery plants and involuntary risks the public faces in normal daily life indicates risks from Dioxin, based on worst case projections, to be several orders of magnitude lower. Thus, the finding of Dioxin does not, in and of itself, constitute an immediate serious public health problem. Granting that the general public will have the final judgement in establishing acceptable levels of trace chemical contaminants, the fact that they are generally uninformed about scientific questions is not sufficient reason to abandon the attempt to introduce more and better science into the body of facts on which final judgements about regulatory limits are based. Further, it is a challenge to better educate the general public with respect to proper use of scientific facts in such a rational process of establishing regulatory limits.

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SESSION I

EPA ACTIVITIES SYMPOSIUM

CHAIRMAN:

D. A. OBERACKER
Environmental Protection Agency
Cincinnati, OH

BEST ENGINEERING JUDGEMENT FOR INCINERATION OF HAZARDOUS WASTES

E. P. CRUMPLER
U. S. Environmental Protection Agency
Washington, DC

ABSTRACT

Incineration is the primary control and disposal tool for hazardous wastes in the 1980's. EPA Resource Conservation and Recovery Act (RCRA) regulations require application of the best engineering judgement (BEJ) approach to the regulatory management of this option. How will designers, equipment manufacturers, and owners/operators interact with EPA? How will permits be written? How often will trial burns be required? How will the performance standards be monitored?

This paper is designed to answer these questions and others which will bear on the success of the engineering application of incineration to hazardous waste disposal.

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EPA OFFICE OF R & D HAZARDOUS WASTE INCINERATION RESEARCH PROGRAMS

E. T. OPPELT
U. S. Environmental Protection Agency
Cincinnati, OH

ABSTRACT

The Environmental Protection Agency's Office of Research and Development supports a number of research and development studies intended to advance the state-of-the-art of hazardous waste incineration. These programs are conducted primarily by the Industrial Environmental Research Laboratory of Cincinnati, Incineration Research Branch and the IERL-Research Triangle Park, North Carolina. This paper describes the Agency's efforts at laboratory, pilot and field-scale, and their relationship to RCRA incineration regulations development and enforcement.

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ENVIRONMENTAL ENGINEERING CONSIDERATIONS FOR HAZARDOUS WASTE INCINERATION

T. W. HUGHES and D. L. ZANDERS
Monsanto Research Corp.
Dayton, OH

D. A. OBERACKER
U. S. Environmental Protection Agency
Cincinnati, OH

ABSTRACT

The U.S. Environmental Protection Agency recently proposed regulations for hazardous waste incineration facilities. The regulations require owners and operators of such facilities to obtain a 99.99% destruction and removal efficiency for the principal organic hazardous components. A technical resource document was prepared by EPA to support the technical aspects of the proposed regulation. The document, "Engineering Handbook for Hazardous Waste Incineration" is discussed in this paper. Topics covered in the handbook include a state-of-the-art survey of incineration and air pollution equipment, waste characterizations, incineration and air pollution control design evaluations, overall incineration facility considerations, capital and operating costs, and trial burn summary data. The engineering handbook provides technical information to be used in the design and performance evaluation of hazardous waste incineration facilities.

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INTRODUCTION

Millions of tons of industrial waste materials are generated each year in the United States. An estimated 57 million metric tons of hazardous waste was generated in 1980. In recent years, incineration has emerged as an attractive potential alternative to hazardous waste disposal methods such as landfilling, ocean dumping, and deep-well injection.

Incineration possesses several advantages which make it a principal disposal technology for hazardous wastes in the future. Some of these advantages are:

- Toxic components of hazardous wastes can be converted to harmless compounds or, at least, to less harmful compounds.
- Incineration provides for the ultimate disposal of hazardous wastes, eliminating the possibility of problems resurfacing in the future.
- The volume of hazardous waste is generally reduced by incineration.

- Heat recovery makes it possible to recover some of the energy produced by the combustion process.

The U.S. Environmental Protection Agency has developed an engineering handbook which serves as a technical resource document for hazardous waste incineration regulations. The handbook is a compilation of information available in the literature and describes current state-of-the-art technology for the incineration of hazardous waste. It is expected that it will be useful as a resource document for Federal, regional, and state EPA officials, designers of hazardous waste incineration facilities; owners and operators of hazardous waste incineration facilities; and the general technical community.

OVERVIEW OF ENGINEERING HANDBOOK CONTENTS

The technical resource draft document is entitled, "Engineering Handbook for Hazardous Waste Incineration". The report contains five major chapters and several appendices which contain background information for the hazardous waste incineration regulations.

Current practices for hazardous waste incineration are detailed in Chapter 2 of the handbook. This chapter contains basic and general information about the nature and operations of the various types of incinerators and air pollution control devices currently used in hazardous waste disposal. Subject matter contained on each fact sheet includes process descriptions, flow diagrams, general operating parameters and process advantages and disadvantages. An overview of emerging incineration technologies is included. Tables 1 and 2 present operating conditions and wastes handled for the incinerators covered in the engineering handbook.

Chapter 3, entitled "Waste Characterization," describes the basic waste analyses required to characterize wastes and discusses how this information is used to match the waste to an appropriate incinerator design and to determine operating conditions. This chapter describes how waste characterization data are used for appropriate incinerator operation; it does not describe how the waste characterization data are to be generated. Hazardous wastes listed under Section 3001 of the RCRA[a] of 1976, regulations are evaluated as to their suitability for incineration. The appropriate incineration technologies are listed for each waste. Table 3 presents the stoichiometric oxygen requirements and combustion product yields for elemental components found in hazardous wastes.

Incineration and air pollution control system design evaluations procedures are contained in Chapter 4. This chapter provides detailed information and procedures for evaluation of incinerator

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[a] RCRA = Resource Conservation and Recovery Act.

TABLE 1. PERTINENT INCINERATION PROCESSES AND THEIR TYPICAL OPERATING RANGES (1)

Process	Temperature range, °F (°C)	Residence time
Rotary kiln	1,500 to 2,900 (820 to 1,600)	Liquids and gases, seconds; solids, hours
Liquid injection	1,200 to 2,900 (650 to 1,600)	0.1 to 2 seconds
Fluidized bed	840 to 1,800 (450 to 980)	Liquids and gases, seconds; solids, longer
Multiple hearth	Drying zone 600 to 1,000 (320 to 540) Incineration 1,400 to 1,800 (760 to 980)	0.25 to 1.5 hours
Coincineration	300 to 2,900 (150 to 1,600)	Seconds to hours
Starved air combustion/pyrolysis	900 to 1,500 (480 to 820)	Tenth of a second to several hours

TABLE 2. APPLICABILITY OF AVAILABLE INCINERATION PROCESSES TO INCINERATION OF HAZARDOUS WASTE BY TYPE [2]

Waste type	Rotary kiln[a]	Liquid injection	Fluidized bed[a]	Multiple hearth	Multiple chamber	Coincineration	Starved air combustion/ pyrolysis	Wet air oxidation	Molten salt
Solids:									
Granular, homogeneous	x		x	x		x	x		
Irregular, bulky (pallets, etc.)	x				x	x	x		
Low melting point (tars, etc.)	x	x[b]	x			x	x		
Organic compounds with fusible ash constituents	x			x		x	x		x
Gases:									
Organic vapor laden		x				x			
Liquids:									
High organic strength aqueous wastes often toxic	x[c]	x				x		x	
Organic liquids	x[c]	x	x			x			x
Solids/liquids:									
Waste contains halogenated aromatic compounds (2,200°F minimum)	x	x[d]	x			x	x		x
Aqueous organic sludges	x[e]		x	x		x		x	

[a] Suitable for pyrolysis operation.

[b] If material can be melted and pumped.

[c] If equipped with auxiliary liquid injection nozzles.

[d] If liquid.

[e] Provided waste does not become sticky upon drying.

TABLE 3. STOICHIOMETRIC OXYGEN REQUIREMENTS AND COMBUSTION PRODUCTS YIELDS

Elemental waste component	Stoichiometric oxygen requirement	Combustion product yield
C	2.67 lb/lb C	3.67 lb CO_2/lb C
H_2	8.0 lb/lb H_2	9.0 lb H_2O/lb H_2
O_2	-1.0 lb/lb O_2	-
N_2	-	1.0 lb N_2/lb N_2
H_2O	-	1.0 lb H_2O/lb H_2O
Cl_2	-0.23 lb/lb Cl_2	1.03 lb HCl/lb Cl_2 -0.25 lb H_2O/lb Cl_2
F_2	-0.42 lb/lb F_2	1.05 lb HF/lb F_2 -0.47 lb H_2O/lb F_2
Br_2	-	1.0 lb Br_2/lb Br_2
I_2	-	1.0 lb I_2/lb I_2
S	1.0 lb/lb S	2.0 lb SO_2/lb S
P	1.29 lb/lb P	2.29 lb P_2O_5/lb P
Air N_2	-	3.31 lb N_2/lb $(O_2)_{stoich}$

Stoichiometric air requirement = 4.31 x $(O_2)_{stoich}$

and air pollution control device design and operating conditions. Basically, this involves a series of internal consistency checks designed to determine whether [1] acceptable temperatures residence times, oxygen concentrations, and mixing can be achieved and maintained in the incinerator, [2] the various components of the system have sufficient capacity to accommodate the quantities of waste to be burned, [3] appropriate air pollution control device operating conditions can be maintained, [4] the design includes process control and automatic shutdown safeguards to minimize release of hazardous materials in the event of equipment malfunction and [5] proper materials of construction are used. Individual evaluation procedures are currently provided for liquid injection and rotary kiln incinerators and for several types of wet scrubbers. Figures 1 and 2 depict types of information considered for evaluation of hazardous waste incineration.

Chapter 5 of the engineering handbook covers overall facility design, operation and monitoring requirements. This section provides the engineering background information on the technical capabilities necessary for the incineration facility to process hazardous waste safely and effectively. The chapter discusses overall facility layouts; equipment requirements common to all facilities; waste receiving equipment, procedures, and storage; personnel safety; emergency procedures and provisions, monitoring procedures and instrumentation; sampling and analysis equipment and methodologies; sources of fugitive emissions and their control;

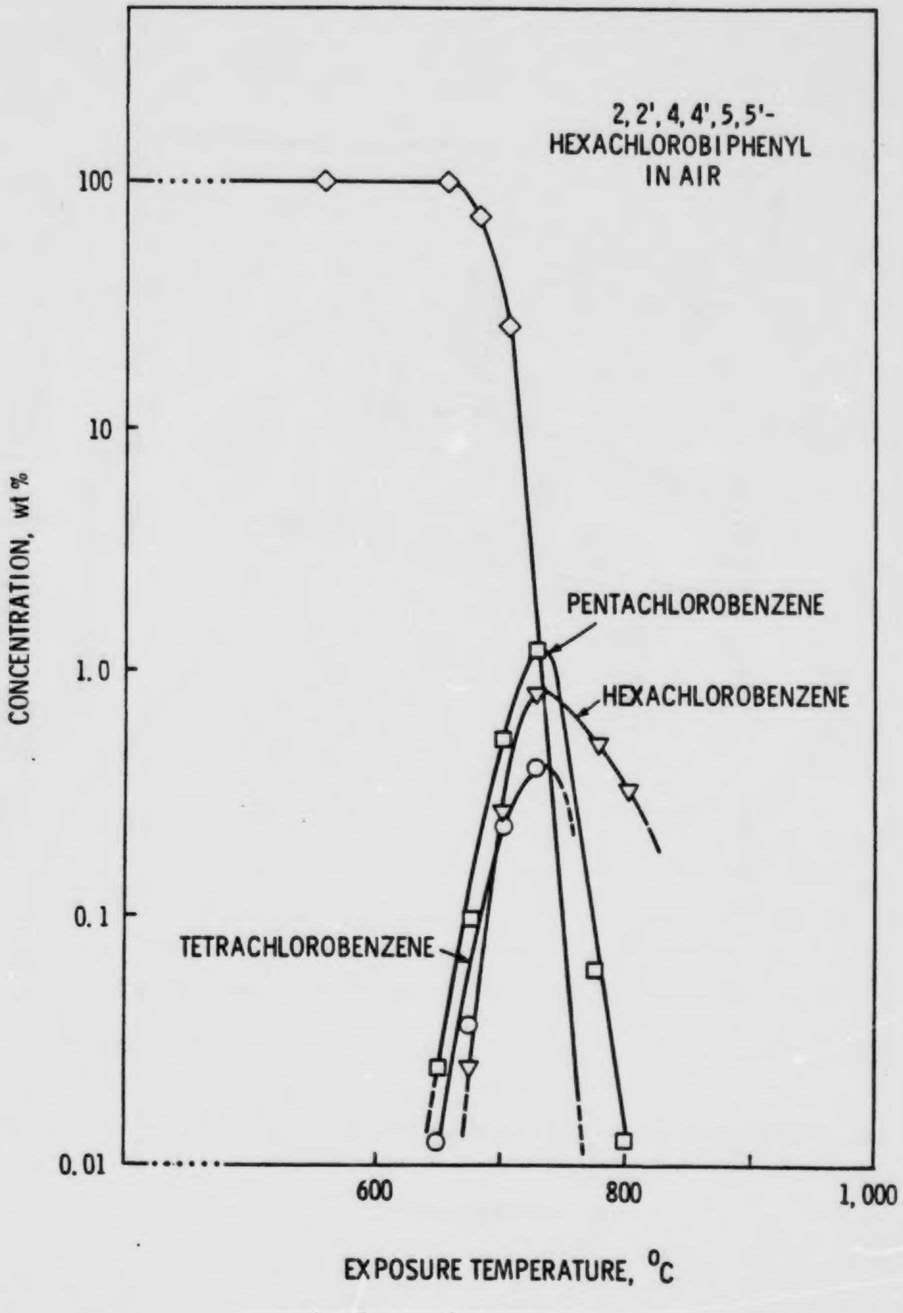

Fig. 1 Decomposition of hexachlorobiphenyl [3].

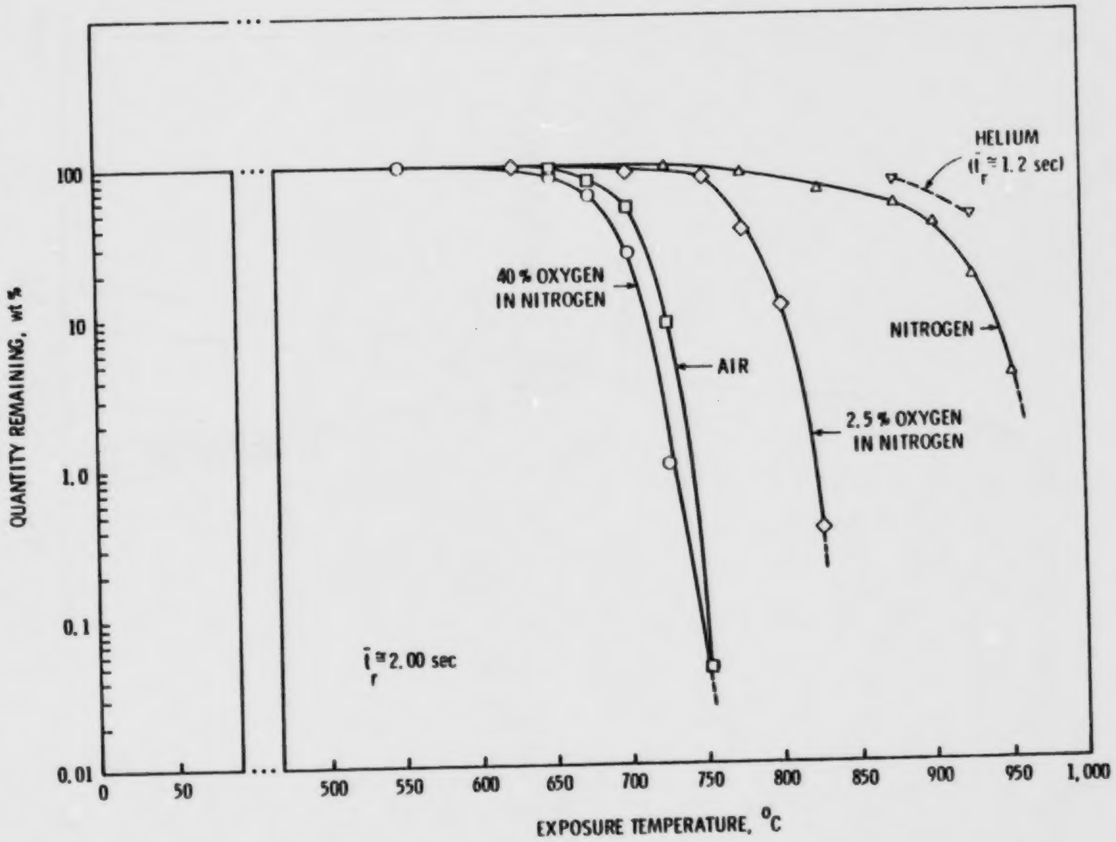

Fig. 2 Decomposition of pentachlorobiphenyl in different gaseous atmospheres [3].

scrubber/quench water handling and disposal; and ash collection systems. Figure 3 presents the recommended locations for continuous monitoring of temperature, combustion product oxygen concentration, and gas flow.

The engineering handbook contains procedures for estimating incineration costs in Chapter 6. This chapter examines the economic factors involved in the construction of new facilities and the operation of existing facilities. Capital costs for incinerators and air pollution control devices are presented. Costs involved in changing incinerator operating conditions (temperature, percent excess air, and residence time) and the removal efficiency of air pollution control devices are examined. The costs involved in performing trial burns are also addressed in this chapter. (The capital and operating are currently being updated.)

The appendices provide a subject index, glossary of terms, tables of conversion factors and a bibliography. Summaries of incineration data obtained at laboratory, pilot and full-scale are tabulated. The incineration data provide an overview of available trial burn data collected by other investigators.

ACKNOWLEDGEMENT

The preparation of Engineering Handbook for Hazardous Waste Incineration required a major, well-orchestrated effort by

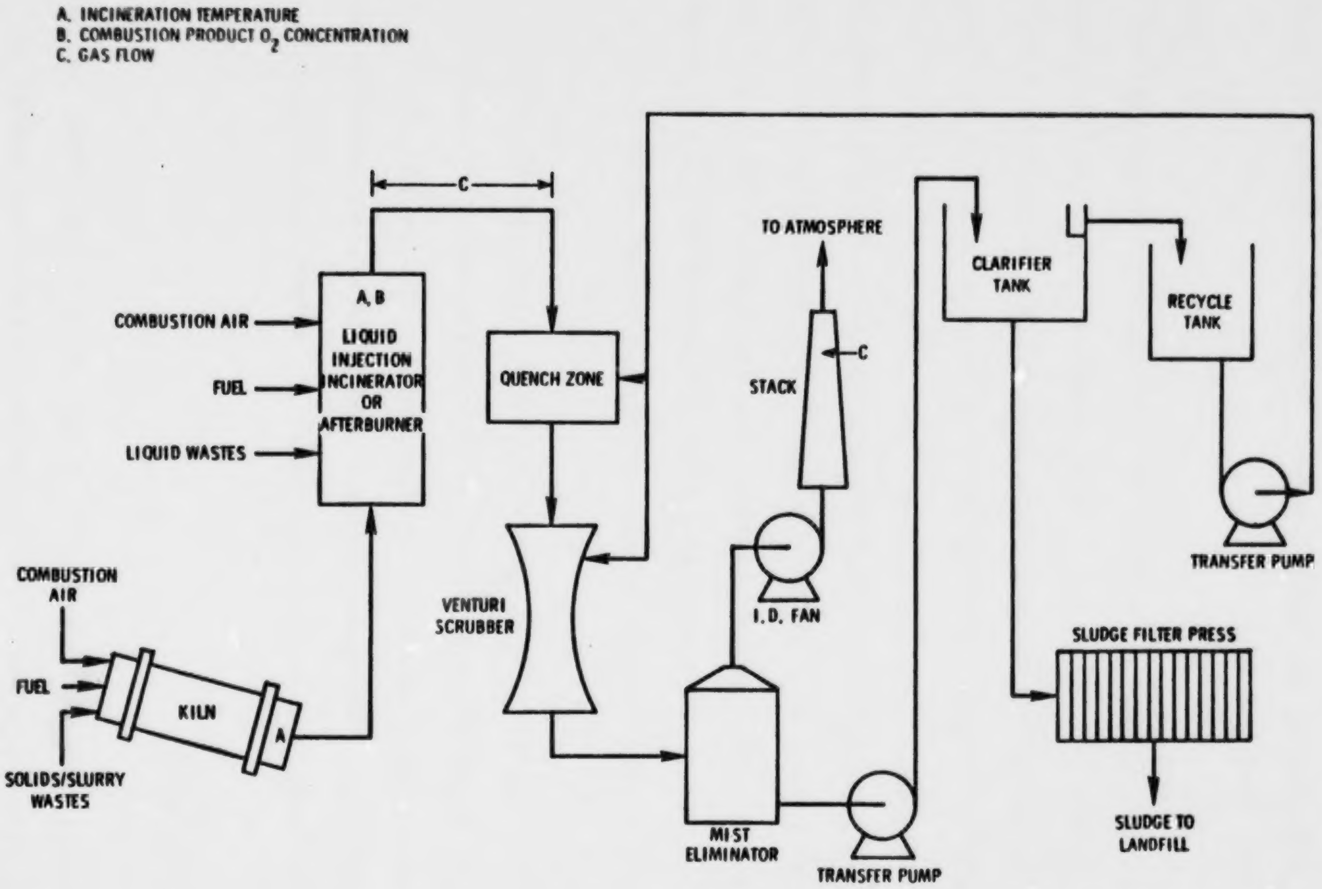
A. INCINERATION TEMPERATURE
B. COMBUSTION PRODUCT O_2 CONCENTRATION
C. GAS FLOW
C
COMBUSTION AIR
FUEL
LIQUID WASTES
A, B
LIQUID INJECTION INCINERATOR OR AFTERBURNER
QUENCH ZONE
TO ATMOSPHERE
STACK
C
CLARIFIER TANK
RECYCLE TANK
COMBUSTION AIR
FUEL
SOLIDS/SLURRY WASTES
KILN
A
VENTURI SCRUBBER
I. D. FAN
MIST ELIMINATOR
TRANSFER PUMP
TRANSFER PUMP
SLUDGE FILTER PRESS
SLUDGE TO LANDFILL

Fig. 3 Recommended continuous monitoring points.

numerous individuals inside and outside the U.S. Environmental Protection Agency. The accelerated nature of the effort necessitated the employment of individuals from six EPA organizations and the utilization of contractor support for the actual composition of the technical materials. The EPA personnel had to serve as the technical critique committee for this effort, even as they were forced to carry their own regular work load. The following EPA organizations contributed staff to work with the Monsanto Research Corporation, A. D. Little, Inc., and TRW, Inc., in the preparation of the manual:

Municipal Environmental Research Laboratory, Cincinnati

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Office of Solid Waste

Region II, New York, NY

Region V, Chicago, IL

The authors would like to express their most sincere thanks to the above groups and their dedicated staff, who produced the document in a genuine team effort.

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THE MARKET FOR INCINERATION CAPACITY

P. G. McCANN
Booz, Allen & Hamilton, Inc.
Bethesda, MD

ABSTRACT

Proponents of incineration believe that it should be encouraged because it is an environmentally safe method of hazardous waste disposal. However, the development of incineration capacity may be constrained by market and regulatory uncertainties. Some companies are taking a "wait and see" approach until these issues are better defined. This paper will discuss the potential for incineration as a waste disposal technology in light of these uncertainties.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has now issued a major portion of the regulations, authorized by the Resource Conservation and Recovery Act (RCRA), to track and control hazardous waste from point of generation to ultimate disposal. These regulations are causing important changes in the waste management practices of many hazardous waste generators. The use of incineration in place of land disposal is certainly one such change that is occurring. However, the rate at which incineration is adopted and the types of incineration capacity that will be needed are still very much in question.

Nevertheless, certain trends are emerging.

- The volume of hazardous waste incinerated will expand substantially.
- On-site incineration will play an increasing role.
- Market and regulatory uncertainty will constrain development of capacity.

Each of these factors is discussed in greater detail in the remainder of this paper.

GROWTH IN INCINERATION

The fact that incineration will continue to expand as a reliable method of managing hazardous waste is generally accepted. However, the rate and timing of this growth have been the subject of some debate. Several factors suggest that hazardous waste incineration will grow substantially and this growth will continue at least over the next five years:

- The RCRA regulations, as promulgated by EPA, seem to encourage incineration over land disposal.
- Liability concerns are motivating firms to choose incineration over other options even when the costs are considerably higher.

Most incineration of hazardous waste occurs on-site. Incineration is widely used in the chemical industry and some of the largest firms operate 20 or more incinerators. Unfortunately, accurate data on on-site incineration is not available. However, based on permit applications, on-site incineration seems to be increasing.

Data on hazardous waste incineration at off-site facilities is available and was collected as part of a survey done by Booz, Allen, for EPA during April and May of 1980.[1] Booz, Allen was asked to provide a snapshot of the capabilities and expansion plans of the commercial hazardous waste management industry.

The study reported that in April 1980, 23 facilities in the U.S. were offering incineration as a waste disposal alternative. It was estimated that these facilities processed almost 400 thousand wet metric tons of wastes considered hazardous (Table 1). This represents about 6 percent of all wastes treated/disposed at commercial facilities (Table 2).

The study for EPA also reported the planned capacity additions for off-site incineration. Even though many of these facilities were operating at less than 60 percent of capacity, very aggressive expansion plans were reported. Commercial waste management firms planned to more than double capacity over the next several years. These firms believed that once the regulations were in place, the demand for incineration would increase sharply. It is important to point out that less than 20 percent of the planned capacity expansions were categorized as firm commitments. The remainder of the additions represented less definite plans such as expansions that were "under study."

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[1] U.S. Environmental Protection Agency, "Hazardous Waste Generation and Commercial Hazardous Waste Management Capacity," Part II "Off-Site Hazardous Waste Management Capacity," Environmental Protection Agency (SW-894), December 1980.

TABLE 1

Commercial Off-Site Facilities in the U.S. by EPA Region

April 1980

EPA Region	Number of Incinerators	1980 Volume of Wastes (Thousand Wet Metric Tons)
I	3	23
II	1	26
III	1	48
IV	7	65
V	6	97
VI	6	98
VII	0	--
VIII	0	--
IX	1	40
X	0	--
TOTAL	25	398

Source: Booz, Allen & Hamilton Inc.

TABLE 2

Estimated Volumes of Hazardous Waste Treated/Disposed At Commercial Facilities By Waste Management Alternative

(1980)

Waste Management Alternative	Volume (Thousand Wet Metric Tons)	Percent of Total
Incineration	398	6
Landfill	2,699	39
Deep Well Injection	788	11
Land Treatment	537	8
Chemical Treatment	2,346	30
Resource Recovery	424	6
TOTAL	7,192	100

Source: Booz, Allen & Hamilton Inc.

It is interesting to note that of all of the off-site capacity additions, incineration had the largest percentage increase in capacity planned (Table 3). This can be contrasted with the most prevalent disposal option, landfill, which shows a probable decrease in annual capacity over the next several years.

These were the capabilities and plans of the industry in April of last year. Because these data were developed before many of the regulations were published, the snapshot of the industry had obvious limitations. Since then, the outlook for the future capacity of the industry has generally worsened. Several large landfills have run into problems with their expansion plans and some others have closed. Therefore, the outlook for landfill capacity is even worse than it was one year ago. Although the very optimistic plans of the industry for expansion of incineration probably will not be realized, the incineration outlook is brighter than for landfills. One major new incineration site, planned by IT Corporation,[1] in Louisiana, has made substantial progress and may begin operation in mid 1982. Presented below are the reasons why incineration may expand at a rate substantially exceeding that of landfills.

---

[1] IT Corporation, "Impact," Vol. 3, No. 1, January, February, March 1981.

TABLE 3

1980 Capacity and Planned Capacity Additions Of the Commercial Hazardous Waste Management Industry

Waste Management Alternative	Annual Capacity (Thousand Wet Metric Tons)	Percent Increase in Capacity Planned by 1983
Incineration	670	122
Landfill	5,675*	8
Deep Well Injection	4,657	0
Land Treatment	2,437	28
Chemical Treatment	3,921	51
Resource Recovery	1,069	20
TOTAL	18,429	18

Source: Booz, Allen & Hamilton

Regulations

Probably the most important reason for the expected rapid growth in hazardous waste incineration is the RCRA regulations. Many industry and government representatives feel that the regulations encourage incineration over landfill. Several aspects of the regulations seem to substantiate this claim:

- Hazardous wastes that are burned on-site for their energy value are not currently part of the RCRA control system. This provides a strong incentive for firms to burn wastes.[1]

- Ignitable wastes will not be able to be land disposed after May 19, 1981 according to proposed regulations. This will force some generators who currently landfill these wastes to shift to incineration.[2]

- The proposed land disposal regulations include a requirement for detailed environmental studies of the long-term effects of the facility that are not required for other types of facilities. The standards to be used are not provided by EPA, and commercial landfill operators view this as an additional barrier to facilities of this kind.[3]

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[1] Federal Register, May 19, 1980, Vol. 45, No. 98, Part 265, p. 33216.

[2] Federal Register, February 20, 1981, Vol. 46, No. 34, Part 265.312, p. 13492

[3] Federal Register, February 5, 1981, Vol. 46, No. 24, Part 264.21, p. 11162.

These three parts of the RCRA management system seem to clearly favor incineration. Furthermore, some states have taken an even more favorable approach to incineration over landfill in developing their regulations.

Liability Concerns

In addition to the direct regulatory incentives to the use of incineration for hazardous waste management, liability concerns stemming from the "cradle to grave" management responsibility are also motivating generators to choose incineration over other disposal options. This is true even when disposal costs are much higher for incineration. Table 4 compares typical prices currently charged by commercial waste management firms for their services. Although prices are highly waste specific, these estimates provide a general understanding of the differences between waste management alternatives. As the table shows, incineration often requires a substantial premium over land disposal from the generator. However, an increasing number of generators are willing to pay this premium. Some large chemical companies have adopted policies to incinerate to the maximum extent possible so that long-term liability concerns are minimized. They are reluctant to land dispose organic wastes which could be incinerated and are also looking for ways to minimize their risks in managing inorganic wastes.

TABLE 4
Typical Prices Charged By Commercial Hazardous Waste Management Firms
(1981)

Waste Management Alternative	Price	Comments
Incineration		
. Liquids	$.25-$3.75/gal	Highly dependent on Btu value
. Solids/sludges	$.20-$1.00/lb	
Land disposal		
. Low hazard	$25-$50/ton	Also depends on whether in bulk or drums
. High hazard	$100-$300/ton	
Chemical/Physical/ Biological Treatment		
. Neutralization	$.10-$.60/gal	Varies widely
. Aqueous Treatment	$.50-$1.20/gal	
. Solvent Recovery	$1.25-$2.60/gal	
Deep Well Injection	$.12-$.50/gal	
Land Treatment	$.02-$.15/gal	

Source: Booz, Allen & Hamilton Inc.

INCREASES IN ON-SITE INCINERATION

A second major trend in the future of hazardous waste incineration is an increasing interest in on-site incineration. There are several reasons why on-site incineration may play a larger role in the future:

- Siting advantages of on-site
- Types of firms who generate incinerable wastes
- Aspects of production control may favor on-site.

There is reason to suspect that on-site incinerators may be easier to site than incinerators at commercial off-site facilities. Public opposition has thwarted the siting attempts of many planned incinerators, both on and off site, but on-site incineration may face considerably less opposition. A frequent complaint of local citizens opposing a hazardous waste facility is that they object to the safety risks of having truckloads of waste shipped through their neighborhoods. This is not a factor for on-site facilities. Another objection of local citizens is often the question of equity. Why should we have to bear all of the burden when the benefits are enjoyed by industries in other communities and even other states? Although generators operating on-site facilities may be producing products for consumption in many states, the benefits of the facility are more directly related to their interests, i.e., employment and taxes. Therefore, public opposition may be less for on-site incinerators.

A second reason why on-site incineration may play an increasing role is related to the types of firms who generate incinerable wastes. Most of the wastes that can be incinerated are generated by the organic chemical, petrochemical, pharmaceutical, and petroleum industries. Generators in these industries are likely to operate their own incinerators. Many of the chemical companies, especially the largest ones, manage between 90 and 95 percent of their wastes themselves. Furthermore, the trend is toward even greater on-site management. These companies want to maintain control over their wastes from cradle to grave to minimize their potential liabilities. These companies also have the technical skills available to operate on-site incinerators.

Finally, there are production-control related reasons why firms may opt for on-site incineration:

- To take advantage of energy recovery
- To prevent potential production interruptions due to strikes by haulers or operating problems at disposal facilities
- To control long-term disposal costs.

CONTINUED UNCERTAINTY

Even though the outlook for hazardous waste incineration is bright, the development of incineration capacity will be constrained by market and regulatory uncertainties. These uncertainties are causing some companies to take a "wait and see" approach to investment.

Market Uncertainties

The supply and demand relationships for hazardous waste incineration have not fully adjusted to the changes brought about by the first phase of the RCRA regulations. The demand for off-site incineration has not yet reached its expected level. Most incinerators only able to burn liquids are still operating at less than full capacity. Rotary kiln incinerators able to burn solids and sludges as well as liquids are generally operating at higher rates of capacity utilization. However, overall capacity at off-site facilities is not being fully utilized and capacity has not expanded according to plans.

Expansion of hazardous waste incineration may also be constrained by a concern over the increasing energy intensity of incineration. As more and more organic liquids such as solvents are recovered, the Btu value of waste to be incinerated decreases. Potential users of incineration are concerned that energy related operating costs will increase.

The role that emerging technology may play in the future adds an additional market related uncertainty in the decision to invest in incineration. The initial investment could be between $7 and $15 million for a commercial incinerator. The large fixed cost component required for a hazardous waste incinerator may take 5 to 10 years to pay back. It is possible that new technology could displace existing technology within this planning horizon. Emerging technologies include incineration-at-sea, thermal destruction in cement and lime kilns, molten salt combustion, and other thermal processes. Substantial capacity additions through any of these technologies could have important impacts on off-site incineration costs.

Regulatory Uncertainties

Uncertainty over the final form and impact of the regulations are also contributing to a wait and see attitude among potential incinerator investors. Two aspects of the regulation are responsible for much of this uncertainty. First, the quantities of waste that will be incinerated is highly sensitive to the exemption of energy recovery operations from the RCRA control system. If EPA decides to more strictly regulate waste burned for energy value, off-site incineration could increase significantly.

A second aspect of the regulation causing uncertainty among potential incinerator investors is the eventual prohibition of land disposal of ignitables. If EPA retains its current position, incineration will undoubtedly increase. However, if EPA decides not to prohibit ignitables from being land disposed, incineration will have a much smaller role to play.

* * * *

Incineration will play an increasing role in hazardous waste management. It will be called upon to dispose of a wider variety of waste streams. Market and regulatory factors are acting to reduce the cost differential between these options, and increasing liability concerns are making more and more generators feel that the extra cost is justified. However, there remain uncertainties that cloud the ultimate potential of this technology.

SESSION 2

RESEARCH SYMPOSIUM

CHAIRMAN:

C. O. VELZY
Charles R Velzy Associates, Inc.
Armonk, NY

CHLORINATED DIBENZO-p-DIOXINS (PCDD) FROM INCINERATION PROCESSES

G. G. CHOUDHRY, K. OLIE and O. HUTZINGER
University of Amsterdam
The Netherlands

ABSTRACT

Reports on the identification and measurements of polychlorinated dibenzo-p-dioxins (PCDDs) and related compounds in effluents from incinerators on the one hand and on experimental pyrolysis of chloroaromatic compounds, mainly in simple laboratory systems, on the other, appear now frequently in the literature.

We have now used existing data in the literature to explain the formation of PCDDs and related derivatives from other chloroorganic compounds and from chemically unrelated organic matter by incorporation of inorganic chlorine. The discussion includes pyrolytic decomposition of chloroaliphatic compounds, formation of PCDDs and polychlorodibenzofurans (PCDFs) from chlorophenols, chlorobiphenyls, chlorobenzenes, chlorodiphenyl ethers and PVC.

The de novo synthesis of PCDDs and PCDFs is discussed from a variety of speculative sources.

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1. INTRODUCTION

Incineration of refuse has been an accepted method of solid waste disposal since the end of the nineteenth century and is gaining in popularity in most industrialized and densely populated countries. In The Netherlands, for instance, where land for disposal is scarce the percentage of refuse which is incinerated has increased steadily from 15% in 1960 to 34% in 1978 as a replacement of land-fill (see Table 1) (1).

Table 1

Different methods of solid waste disposal in the Netherlands
(in % of population served by the method indicated)
(1)

Method / year	1960	70	71	72	73	74	75	76	77	78
incineration	15	20	20	26	26	26	30	30	30	34
composting	17	13	15	13	18	18	18	18	19	21
land-fill	68	67	65	61	56	56	52	52	51	45

During incineration, the bulk of the refuse is reduced to about one third and the solid end products, slag and fly ash are sanitary and easy to handle. In the incineration process, raw municipal refuse is fed into furnaces at temperatures between 800 and 1100°C the lower and upper limits of temperature being determined by incomplete combustion and appearance of odorous combustion gases below 800°C on the one hand and the liquefaction of slag at temperatures above 1100°C on the other.

The principal combustible components of refuse entering a municipal incinerator include various paper products, textiles, wood, leather and rubber. Most incinerators yield four end products, which may possibly contaminate the environment: slag, quench-water used for cooling the slag, fly ash collected in electrostatic precipitators or similar devices and the gaseous emissions commonly referred to as flue gas (Figure 1).

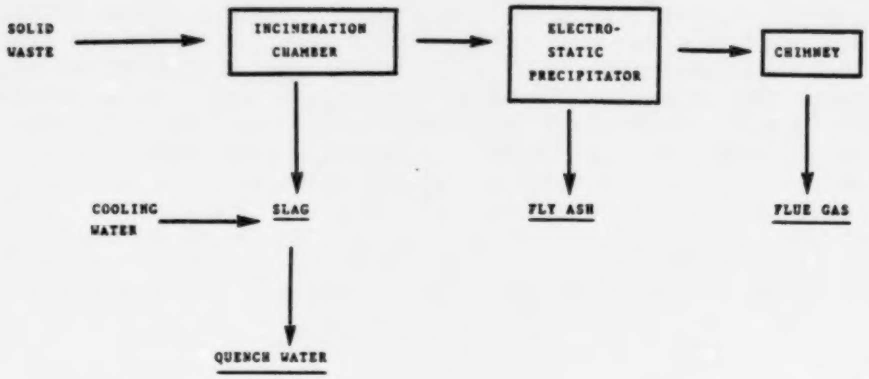


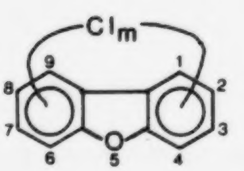
Fig. 1. Schematical presentation of the incinerator process. (End-products are underlined).

The refuse, when decomposed in a furnace yields gases such as nitrogen oxides, sulfur oxides, carbon monoxide, and hydrogen chloride in reasonably large amounts and these are often referred to as macropollutants. Such gases emitted during the incineration of municipal refuse generally enter the atmosphere directly. Airborne particulates may also be released with gaseous emissions and may comprise approximately 20% by weight of the total incinerator emissions. Such emissions have been strictly regulated and can be reduced through the application of venturi scrubbers, electrostatic precipitators, cyclone scrubbers and other devices for similar treatment of incinerator effluent. Most modern municipal incinerators have air pollution abatement equipment, mainly electrostatic precipitators, in which > 98% of all particulate matter is retained.

One ton of refuse yields, on the average, 250 kg slag for which 3500 lt water is used; 30 kg fly ash and 7000 m^3 of flue gas containing: 3.5 kg CO, 0.05 kg HF, 1.3 kg NO_x, 1.65 kg SO_x, 3.15 kg HCl and 0.66 kg particulate matter.

In addition to installations which cater to the burning of municipal refuse, there are incinerators specially developed for the combustion of chemical waste and, when considering combustion processes generally, attention has to be paid to fossil fuelled powerhouses, car and diesel truck exhaust and a number of industrial processes.

While water, carbon dioxide and the higher oxidation states of some other elements are the main products of combustion of natural organic material, no commercially used incineration equipment oxidises organic materials completely and effluents or residues from burning processes contain organic material of varying complexity derived from either incomplete combustion or thermal synthesis. A good example of the latter is the pyrolytic formation of polycylic aromatic hydrocarbons (PAH's) in all processes which involve burning of coal, oil, gasoline or refuse (2). During the last three years, new types of compounds namely polychlorinated dibenzofurans (PCDF's) (1) and polychlorinated dibenzo-p-dioxins (PCDD's) (2), from effluents of incineration processes, have received considerable attention. The reason of this is that some of these tricyclic aromatics exhibit extreme toxicity (3,4,5,6,7,8) and that combustion effluents might be a ready mechanism of distributing them in the environment of densely populated areas. In the past, we have identified PCDF's and PCDD's in the flue gas and fly ash from some municipal incinerators in The Netherlands (9,10,11). Buser et al. (12) claimed similar identifications in samples from municipal incinerators in Switzerland. Recently, Eiceman, Clement and Karasek (13) have carried out the analysis of fly ash collected from municipal incinerators located in major urban centersin Japan, The Netherlands and Canada. They could detect at trace levels approximately 100 organic compounds which include PCDD's, PCDF's, polychlorinated phenols, polychlorinated benzenes, polycyclic aromatic hydrocarbons, phthalate esters and aliphatic hydrocarbons.



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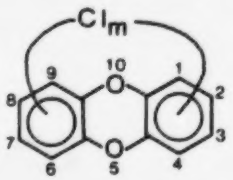


2

m = 1-8

Some results of analyses of PCDF's and PCDD's along with other chlorinated compounds such as chlorophenols (Cl-phenols), chlorobenzenes (Cl-benzenes), polychlorinated biphenyls (PCB's) etc. found in fly ash emitted from the incinerators are documented in Table 2.

Table 2

Results of analyses[a] of chlorinated compounds in fly ash

Ref.	Type of incineration[b]	Sample[c]	Detected compounds	Remarks
11	m.w.	A,B	Cl-phenols PCDDs, PCDFs	
12	m.w.	A,B	PCDDs, PCDFs	found PCDF-pattern is comparable with PCB-pyrolysis results
14/15	m.w. c.w.	A,B		samples taken at various temperature in oven and stack: 900, 480 and 260°C
16	-	C	Cl_4-phenol Cl_5-phenol	
17	m.w.	B	PAH	
18	m.w.	A	Cl-benzenes	many different chlorinated compounds detected
19	m.w.	A	Cl-benzenes	only presence of chlor. benzenes was studied
20	m.w.	A,B	PCDDs, PCDFs	
13	m.w.	A	aromatics, PCDDs Cl-benzenes	
21	m.w.	A,B	PCDDs, PCBs	
22	m.w.	A,B	Cl-benzenes PCDDs, PCDFs	

[a] Analyses were conducted on gas chromatograph-mass spectrometer (GC-MS) unit.

[b] m.w. municipal waste c.w.: chemical waste

[c] A: fly ash from electrostatic precipitator B: fly ash, stack-collected
C: airborne particulate matter from a residential town area, 600 m^3 of air sampled

In the past, PCDD's and PCDF's have taken part in several accidents. These pollutants have caused severe intoxications e.g. "Yusho" in south-west Japan in 1968, and environmental contaminations as in Seveso, Italy in 1976.

The unexpected findings of the two tricylic aromatics namely PCDF's and PCDD's in the effluents from the incinerators raise some questions. Are PCDD's and related compounds produced thermally in the incinerators? What are the mechanisms for the thermochemical formation of these undesired chloropollutants? What is the source of chlorine? Whether organochlorine species present in the waste mixtures are wholly responsible for the appearance of the chloroorganics in the incineration process or inorganic chlorine also acts as a source of chlorine? If the latter does happen, what is the mechanism through which inorganic chlorine enters into the organic compounds?

Experimental research work including analysis of flue gas and fly ash from incinerators as well as laboratory pyrolysis of precursors of PCDD's and related pollutants appears frequently in the literature. Quite recently, a review article about PCDD's and related compounds in incinerator effluents has been published by Lustenhouwer, Olie and Hutzinger (22). They have discussed very briefly some possible mechanisms for thermal generation of these chemicals. So far as our information is concerned, no other author has tried to treat this subject theoretically in order to search some answers to the above raised questions. Therefore, we have attempted to write mechanisms for the thermal formation of polychlorinated dibenzo-p-dioxins and related compounds.

The present preliminary article is divided into three main parts. In the first part, thermochemical decompositions of chlorinated monomers and polymers e.g. poly(vinyl chloride) (PVC) and lignins are covered. The subsection dealing with chloromonomers includes aliphatic and aromatic compounds as well as thermal production of dibenzofurans and dibenzo-p-dioxins.

During the thermolysis of organic matter, incorporations of chlorine from inorganic chlorides, with the resultant formation of chloroorganic compounds e.g. methyl chloride and possibly CCl_4 and hexachlorobenzene are mentioned in the second part. In the final major part, hypotheses about the thermal formation of polychlorinated dibenzo-p-dioxins and related compounds in the incinerators, formulated on the basis of literature data, are discussed.

2. THERMOCHEMICAL DECOMPOSITION

The thermochemical fate of two types of compounds namely: i) chloromonomers, and ii) polymers has been dealt within this major section. We have discussed chloromonomers in detail. A brief attention has been paid to the thermodegradation of polymers.

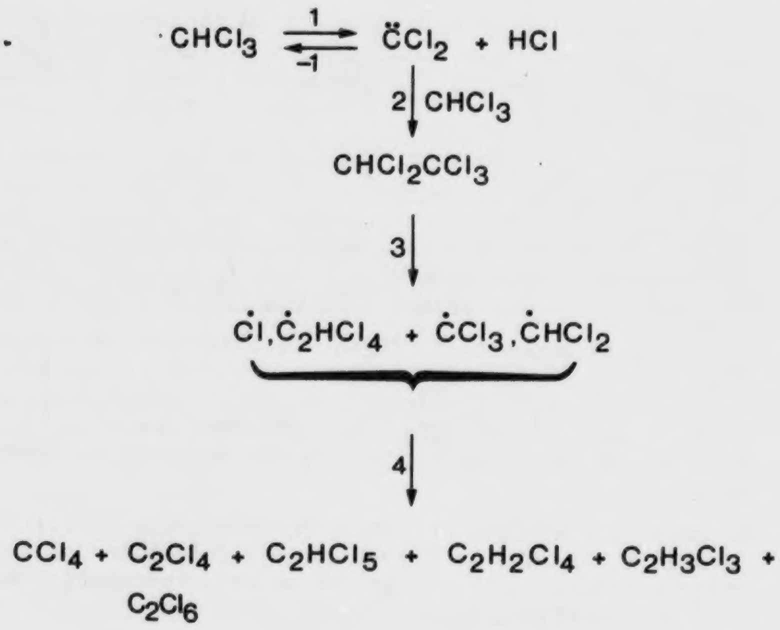
2.1. Chloromonomers

We will discuss chloromonomers under three arbirary headings; which include: a) aliphatics, b) aromatics, and c) generation of dibenzofurans and dibenzo-p-dioxins. Pollutants like polychlorinated dibenzofurans (PCDF's) and polychlorinated dibenzo-p-dioxins (PCDD's), due to their recognized toxic effects (3,4,5,6,7,8), are of prime interest and concern to a large majority of environmental chemists. That is why, instead of treating PCDF's and PCDD's along with other aromatics, these chloropollutants will be described under a separate heading.

2.1.1. Aliphatics

At 800°K for contact time of approximately 0.4 min, the chief products of the decomposition of chloroform ($CHCl_3$) in an atmosphere of helium are HCl (41%) and tetrachloroethylene (C_2Cl_4) (13%) together with other products such as C_2Cl_6 (3%), C_2Cl_5H (0.7%), C_2Cl_3H (0.5%), CCl_2H_2 (0.8%) and $C_2Cl_4H_2$ (0.3%) (23). With the support of previously published data (23,24,25) and their own observations, Murgulescue and Weissman (26) formulated a correct mechanism for the pyrolysis of chloroform, which is given below (Scheme).

Scheme



Chloroform decomposes reversibly to produce dichlorocarbene ($\ddot{C}Cl_2$) and HCl (step 1). The intermediate CCl_2 species react further with chloroform, probably, through insertion in the C-H bond with the resultant formation of C_2HCl_5 (step 2). Pentachloroethane disintegrates under these conditions to give radical species (step 3). The radicals generated via step 3 continously form higher chlorinated compounds by recombination, substitution and atom abstraction (step 4) (26).

By heating at 405^{o}C for 5 months any perchlorocarbon compound or mixture of compounds having an over-all mole ratio of chlorine to carbon between one and four, an equilibrium (Reaction 1) is reached in a closed condensed fluid system between hexachlorobenzene (C_6Cl_6), carbon tetrachloride (CCl_4), and smaller amounts of hexachloroethane (C_2Cl_6) (27).

$$9\ C_2\ Cl_6 \rightleftarrows 12\ C\ Cl_4 + C_6\ Cl_6 \tag{1}$$

The equilibrium constant for the stoichiometric Reaction 1 is given by:

$$K_1 = \frac{(CCl_4)^{12}\ (C_6Cl_6)}{(C_2Cl_6)^9} \tag{2}$$

The average value of K_1 obtained from the experiments on equilibrium rearrangement of some perchlorocarbons namely C_2Cl_4,C_2Cl_6,C_3Cl_6 (hexachloropropene), C_4Cl_6 (hexachlorobutadiene) and mixture of CCl_4 and C_6Cl_6 is 2.7 x 10^{11}, with a standard deviation of 1.4 x 10^{11}.

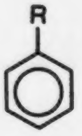
The extreme sensitivity of the equilibrium expression (Eq. 2) to errors in the concentrations of CCl_4 and C_2Cl_6 is undoubtedly partly responsible for the large standard deviation (27). That Reaction 1 (or Eq. 2) is indeed a true equilibrium condition is demonstrated by approaching it from both sides. Thus C_2Cl_6 and a 12:1 mixture of CCl_4 and C_6Cl_6 give essentially the same mixture at equilibrium (27).

It should be added that, through sealed tube pyrolysis starting from additional perchlorocarbons such as C_3Cl_6(cyclo), n-C_4Cl_8, C_5Cl_6 (cyclodiene), C_5Cl_8(cycloene), $C_{10}Cl_{12}$ (pentacyclo), and a mixture of Cl_2 + C_6Cl_6,Grant (28) has confirmed the establishment of the equilibrium (Reaction 1), previously observed by Aubrey and van Wazer (27).

On passing a mixture of carbon tetrachloride (CCl_4) and hydrogen gas through a hot tube at 600-650^{o}C, hexachlorobenzene (60%) and tetrachloroethylene (35%) are gained as major products; hexachloroethane (5%) and trichloroethane ($CH_3.CCl_3$) (0.01%) being formed as minor ones (29).

2.1.2 Aromatics

Kislitsyn, Savinykh and Latysheva (30) reported that the thermal decomposition of anisole (3; R = OCH_3) at 530°C for contact time of 1.77 sec provides a large number of liquid products which include benzene, toluene, phenol, benzaldehyde, acetophenone, biphenyl, phenyl benzyl ether (3; R = -H, $-CH_3$, -OH, $-\overset{H}{\underset{O}{C}}$, $\overset{CH_3}{\underset{O}{C}}$, $-C_6H_5$, $-OCH_2C_6H_5$; respectively), m- and p-xylene (4; R = m-, p- CH_3), o-, m- and p-cresol (4; R = o-, m-, p-OH) and formaldehyde (H_2CO).



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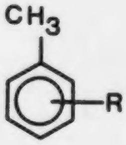

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Main products were phenol (3; R = -OH) (34-47%) and benzeldehyde (3; R = -CHO) (25-28%). It is noteworthy that benzene (3; R = H) and o, m- and p-cresols (4; R = OH) appeared as pyrolytic products of appreciable amounts (2.6 - 11.1%). The gaseous products of this pyrolytical process included methane, carbon monoxide and hydrogen; CH_4 being principal product (30).

The thermolysis of long chain acetoxy-alkylbenzene and hydroxy - alkylbenzene derivatives at 340-350°C affords products in which acetoxy or hydroxy groups and/or alkyl residues are substituted by hydrogen (31). The yields vary with type, number, and position of substituents on benzene (31).

Furthermore, the thermal cracking of phenol (3; R = -OH) and o- and p-cresol (4; R = o-, p- OH) at atmospheric pressure for contact time of 2.5 sec leads to the formation of products arising due to reductive dehydroxylation and demethylation (32). It is noteworthy that, in addition to these products, thermal cracking of phenol and of 4 (R = o, p- OH), for instance at 780°C provides dibenzofuran with a molar yield amounting to 0.37 - 1.54 (32).

Chain chlorination of aromatic compounds for instance benzene can be depicted by two types of mechanisms (33) including a) addition mechanism, which proceeds via an intermediate cyclodiene compound and b) abstraction mechanism, which takes place through the intermediary of phenol radicals. When the concentration of chlorine (Cl_2) gas is one atm., it is found that at 450°K the possibility of either mechanism is about equal (33). However, at higher temperatures the trend is towards the abstraction mechanism while low temperature favor the addition (33).

The nature and yields of pyrolytic products of monochlorobenzene (3;

R = Cl) depend upon the temperature of pyrolysis (34,35,36). A few years ago, Louw, Rothuizen and Wegman (36), carried out extensive studies on the thermolysis of chlorobenzene (3; R = Cl) alone and in the presence of additives such as chlorine gas, formaldehyde, azobenzene (PhN = NPh), and allyl benzoate (PhCOO $CH_2CH = CH_2$) at ca. 500°C by employing reactor system, which was operated at atmospheric pressure with nitrogen as the carrier gas. Chlorine gas and formaldehyde were used as sources of Cl and H atoms, respectively; whilst, the other two additives acted as sources of phenyl radicals ($\dot{C}_6H_5$, $P\dot{h}$).

Biphenyl (C_6H_5 - C_6H_5) (3; R = C_6H_5), all isomers of chlorobiphenyls (ClC_6H_4-C_6H_5), and of dichlorobiphenyls (ClC_6H_4 - C_6H_4Cl) along with minor amounts of naphthalene were identified amongst the reaction products of thermal decomposition of 3 (R = Cl). The residence time for these experiments was 110 sec. Both the amount and the composition of the biaryls formed were markedly influenced by the additives. For instance, the proportion of biarlys formed, (ClC_6H_4 - C_6H_5): (ClC_6H_4 - C_6H_4Cl) were 0.08,0.23, 0.9, 1.3 and > 10 in the presence of chlorine, none, formaldehyde, azobenzene and allyl benzoate, respectively (36). These facts strongly point to free radical mechanisms throughout. It is noteworthy that o-, m- and p-$\dot{C}_6H_4Cl$ radicals formed by abstraction of H atoms from 3 (R = Cl) by $Cl^{\bullet}$ and by $H^{\bullet}$(more significant in the presence of formaldehyde) were approximately in the ratio of 20/55/25 (36). The isomer distribution of chlorobiphenyls (ClC_6H_4. C_6H_5) and of dichlorobiphenyls (ClC_6H_4.C_6H_4Cl) in the presence of different additives under the present conditions (ca. 500°C, N_2), although somewhat varying, were of the same type. This observation essentially shows that chlorophenol radicals ($\dot{C}_6H_4Cl$) are isomerically stable under these conditions (36). It should be added that Louw, Rothuizen and Wegman (36) proposed that naphthalene as product of thermolysis of 3 (R = Cl) is formed through the intermediacy of o-chlorophenyl radicals.

It seems interesting to cite herein that addition of $P\dot{h}$ to arene is reversible at 500°C (37,38); consequently, biphenyl may also react with $H^{\bullet}$ to give benzene and $Ph^{\bullet}$ (phenyl radical) under the present conditions (discussed in the preceding paragraph).

Moreover, H atom reactions with substituted benzenes are almost insensitive to substituent effects (39).

2.1.3 Generation of Dibenzofurans and Dibenzo-p-Dioxins

Polychlorinated biphenyls (PCB's) have unique chemical and thermal stability. They were used as heat transfer and hydraulic fluids, lubricants, plasticizers and additives to waxes, dyes and paint. PCB's are mixtures of about 100 individual chlorobiphenyl compounds. They are now the most abundant chlorinated pollutants in the environment and have been distributed throughout the biosphere and became ubiquitous components of environmental samples. Since 1970, the use of PCB's is mostly restricted to closed systems in electrical applications such as transformers and capacitors. However, the disposal and repair of such systems can still result in environmental contaminations. Polychlorinated biphenyls (Cl_n-PCB; n = 4,5,6,7,8) were reported as sources of PCDF's during pyrolysis, as summarized in Table 3. The formation of PCDF's is shown to be substantial. In this process the presence of oxygen is necessary (41). Mechanistic aspects of oxidation have not been investigated but thermal generation of atomic oxygen is probably involved: the authors mention formation of polychlorinated hydroxy biphenyls that can cyclize to form furans (40). It should be added that thermal cyclization of chlorinated 2-phenoxyphenols is well known (43).

PCDF's are most probably formed by intramolecular cyclization (12,40, 41,42). Formation of PCDF's has been proven to occur by four routes. The intramolecular nature of these processes is indicated by the fact that pyrolysis of a known mixture of PCB's does not result in the formation of PCDF's other than those formed during pyrolysis of the chlorobiphenyls separately (41). Furthermore, in addition to the formation of PCDF's, the formation of penta- and hexa-chlorobenzene is also observed with both 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyls at temperatures of 650°C (0.05%) and 700°C (0.5 - 1.0%) (41).

About 150,000 tons of chlorophenols are produced annually for use as wood preservatives (fungicides), as slimicides in paper-mills, bactericides in cutting fluids and industrial oils, as herbicides and as starting materials for a series of other products like the chlorinated phenoxy acids 2,4-D and 2,4,5-T. Chlorophenols contain a variety of contaminants and byproducts. In addition to other chlorophenols, they may contain up to several percent of polychlorinated phenoxyphenols (chloro hydroxy diphenyl ethers). Polychlorinated dibenzo-p-dioxins (PCDD's), dibenzofurans (PCDF's) and diphenyl ethers often are present in the range of ten to hundreds of ppm.

In the last ten years formation of PCDD's during combustion and pyrolysis of chlorophenates was reported. Some results are presented

Table 3

Results of pyrolysis of PCBs

Chlorobiphenyl studied	Process	Product(s)	Yield	Remarks	Ref.
18 different chlorobiphenyls containing 4,5,6,7 and 8 Cl atoms	pyrolysis in air	PCDF	0.1-1%	PCDF-isomers formed according to proposed reaction mechanism	40
2,2',6,6'-Cl_4-PCB 2,2',4,4',5,5'-Cl_6-PCB	pyrolysis in air	PCDF	ca. 2%	formation according to proposed reaction mechanism	12
2,2',4,4',6,6'-Cl_6-PCB Aroclor 1245 and 1260		2,3,7,8-TCDF*	ca. 2%	important formation of 2,3,7,8-TCDF during Aroclor pyrolysis	
2,2',6,6'-Cl_4-PCB 2,2',4,4',5,5'-Cl_6-PCB 2,2,4,4',6,6'-Cl_6-PCB Aroclor 1254	pyrolysis in air	PCDF		pure PCB-isomers did not contain any detectable PCDF	41
Aroclor 1248	pyrolysis in air in O_2 in N_2	PCDF	300 ppm 1100 ppm 2 ppm	presence of O_2 is necessary for the formation of PCDF	42

*2,3,7,8-TCDF indicates 2,3,7,8-tetrachlorodibenzofuran .

in Table 4.

Formation of PCDD's takes place during pyrolysis or combustion of chlorinated phenols. In this case absence of oxygen stimulates the production of PCDD's (48). This indicates that the yield of PCDD's is the net result of thermal decomposition of polychlorinated phenols to H_2O, CO_2 etc. and the thermal formation of PCDD-precursors. From a mechanistic point of view, three possible routes are suggested:

a. dimerization of chlorophenates directly to PCDD's (44,45,46,48,51) including Smiles rearragement (44,45);
b. dechlorination of higher chlorinated PCDD's (44,45);
c. cyclization of chlorohydroxydiphenyl ethers already existing as contaminants in chlorophenates (44).

Route a is by far the most important. In this way it is even possible to prepare pure PCDD-standards by pyrolysis of pure polychlorinated phenates (45,46,55).

It is known that on heating pentachlorophenol, hexachlorobenzene (C_6Cl_6) (51%) and octachloro dibenzo-p-dioxin (OCDD) (6%) is obtained (51). But the pyrolysis of potassium salt of this chlorophenol yields mainly OCDD (51). According to Sandermann, Stockmann and Casten (51), on the one hand, two molecules of pentachlorophenol react to eliminate a molecule of water; thereby decachloro diphenylether being generated. This intermediate ether is then attacked by HCl to produce hexachlorobenzene and the starting phenol. On the other hand, two molecules of pentachlorophenol lose two molecules of HCl; thus OCDD is formed.

The use in forestry and agriculture of products derived from 2,4,5-trichlorophenoxy acid (2,4,5-T) has given rise to much concern in recent years. The major cause of this concern rose from the findings of the highly toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) as a contaminant in many of these preparations. The formation of 2,3,7,8-TCDD during combustion of 2,4,5-T is a matter of controversy. The latest results on this matter suggest that PCDD's are less likely to be formed from 2,4,5-T-derivatives during combustion than from polychlorinated phenols. Some results of the pyrolysis and burning of 2,4,5-T-derivatives under various conditions are summarized in Table 5.

No work on mechanistic aspects of this pyrolysis has been published. It is striking that the yield during combustion of salt- and ester-formulations is higher than during pyrolysis of the free acid (57,59), if TCDD is a pyrolysis product of the free acid at all (53,57).

In brief, laboratory studies reporting on the thermal formation of polychlorinated dibenzo-*p*-dioxins (PCDD's) from chlorinated 2-phenoxyphenols have been published (43). Recently, Lindahl, Rappe and Buser (60) have reported that PCDD's and PCDF's could be formed in relatively important proportions (0.1 - 1.3% and 0.7 - 4.5%; respectively) in the course of pyrolysis of eight isomers of polychlorinated diphe-

Table 4

Results from chlorophenol pyrolysis

Chlorophenols studied	Process	Product(s)[a]	Yield	Remarks	Ref.
mixture of tri-,tetra- and pentachlorophenols	open fire on birch-leaves and wood wool in glass	various PCDDs	1-350 ppm	used mixture was unpurified trade product which contained: phenoxyphenols (0,2-0,5%) and various PCDDs (20-150 ppm)	44
2,4,6-trichlorophenol pentachlorophenol	open fire open fire	TCDD OCDD	2100 ppm 700 ppm		
various tri-,tetra-, and pentachlorophenols separately and in mixtures	pyrolysis	various PCDDs, according to proposed reaction-mechanism	3-10%	PCDDs thus formed were used as standards in PCDD-analysis	45
various polychlorinated phenols	pyrolysis	various PCDDs		PCDDs thus formed were used as standards	46
pentachlorophenol	combustion; pilot scale full scale	no formation of OCDD perhaps formation of OCDD		used clean-up procedure was not effective. large number of compounds interfered in analysis of PCDDs, according to authors	47
trichlorophenol	pilot scale combustion on woodchips	mainly TCDD	230 ppm	addition of copper-salts decreased formation of PCDDs	48
tetrachlorophenol pentachlorophenol		mainly HCDD OCDD	350 ppm 15 ppm	temp. and %-O_2 were varied	
pentachlorophenol	combustion on woodchips	mainly H7CDD OCDD	10.000 ppm 5.000 ppm	starting material contained some nonachlorohydroxy diphenyl ethers	49
tetrachlorophenol pentachlorophenol	pyrolysis	TCDD, HCDD H7CDD		retention time of one of the HCDD found showed resemblance with that of the "chick oedema-factor"	50
pentachlorophenol	pyrolysis	$C_{12}O_2Cl_8$		preparative scale	51
2,4,5-trichlorophenol	exessive heating during accidents	2,3,7,8-TCDD		during production of 2,4,5-trichlorophenol or 2,4,5-T	52
2,4,5-trichlorophenol 2,4,6-trichlorophenol 2,3,4,6-tetrachlorophenol	pyrolysis	2,3,7,8-TCDD 2,4,7,9-TCDD 1,3,4,6,8,9-HCDD	1% up to 15% 30%		53
pentachlorophenol		OCDD	80%		
pentachlorophenol	combustion of treated wood	no PCDDs		slight decrease of original OCDD level	54
pentachlorophenol	combustion of treated paper	no PCDDs		slight decrease of original OCDD level	
Na-pentachlorophenate	combustion of treated paper	OCDD		slight increase of OCDD-level	

[a] Symbols like TCDD, HCDD, H7CDD and OCDD indicates tetra-, hexa-, hepta- and octachlorodibenzo-p-dioxins.

Table 5

Results from pyrolysis of 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and related compounds.

2,4,5-T derivative studied	Process	Product(s)*	Yield	Remarks	Ref.
2,4,5-T	pyrolysis, temp. up to 350 °C			no condensation took place due to decomposition of 2,4,5-T at 350 °C	53
Na-(2,4,5-trichlorophenoxy)-propionate	pyrolysis, 500 °C	2,3,7,8-TCDD	1%	pyrolysis of the free acid did not result in 2,3,7,8-TCDD formation	57
2-butoxyethyl trichlorophenoxy acetate	pyrolysis	2,3,7,8-TCDD	1-3 ppm	combustion of untreated woodchips resulted in high PCDF-background	58
2,4,5-T, ester formulation	combustion on grass open fire	 2,3,7,8-TCDD 2,3,7,8-TCDD	 1,5 ppm 1,4 ppm		59

*2,3,7,8-TCDD indicates 2,3,7,8-tetrachlorodibenzo-p-dioxin.

nyl ethers (PCDPE's) containing 3-6 and 8 chlorine atoms; the temperature of pyrolysis being 600°C.

Quite recently, Buser (61) reported on the pyrolyses of tri-, tetra- and pentachlorobenzenes, carried out in sealed quartz mini-ampoules at 620°C in the presence of air. Chlorobenzenes with a high degree of chlorination than the compounds used for pyrolysis were observed in all pyrolyzates e.g. tetra- and penta from trichlorobenzenes, penta- and hexa-from tetrachlorobenzenes, and hexa- from pentachlorobenzene. The formation of chlorobenzenes with a lower degree of chlorination than the starting material utilized for thermolysis was not observed (61). In addition to chlorobenzenes, mass spectral analyses of the pyrolyzates revealed the presence of other chlorinated compounds which include PCDF's, PCDD's, chlorophenols and in some cases polychlorinated naphthalenes (mainly hepta- and octachloro), polychlorinated styrenes (hepta- and octachloro) and polychlorinated biphenyls (PCB's). PCDPE's and polychlorinated biphenylenes were not observed (61). The yields of polychlorinated dibenzofurans (PCDF's) and dibenzo-p-dioxins (PCDD's) obtained as a result of pyrolytical decomposition of chlorobenzenes are recorded in Table 6.

As seen in Table 6, in the case of the PCDD's, the amounts formed in these pyrolyses were smaller than the amounts of PCDF's. However, substantial amounts of PCDD's (hexa-, hepta- and some octa-CDD) were still observed from the tetrachlorobenzenes and from the combined chlorobenzene sample (tetra- to hepta CDD's). It is noteworthy that in the complex isomeric mixtures, in addition to several other isomers containing 4-8 chlorine atoms, the knowntoxic isomers of PCDF's and PCDD's namely 2,3,7,8-tetra-, 1,2,3,7,8- and 2,3,4,7,8-penta-CDF and 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,6,7,8- and 1,2,3,7,8,9-hexa-CDD were also present but not as principal components (61).

2.2. Polymers

A large number of commerically available synthetic polymers are commonly used in daily life. In terms of tonnage, poly(vinyl chloride) (PVC) is (with polyethylene and polystyrene) one of the three most important plastics currently in use.

PVC, the first fully-synthetic material is now produced over fourty years and its use is still increasing. The largest use of PVC products is in the construction industry mainly for pipelines for drinking water and effluents, in electrical installations, ventilation, drums and roof gutters. PVC is also used in packing such as foils, bottles and other thermoformed products. The automobile industry also needs large mounts of PVC for seat covering, tires and cables.
Most of the products will, sooner or later, appear as waste products, and be subjected to industrial or municipal incineration. The main pyrolysis products of PVC are HCl, CO and CO_2, but some aromatic and aliphatic compounds are also found. Table 7 summarizes some studies on the pyrolysis of PVC.

Table 6

Formation of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) from the pyrolysis[a] of chlorobenzenes at 620°C. (Reproduced from Buser (61)).

	PCDFs formed (ng/sample)				
Compounds	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes[b]	400	1100	550	50	<5
Tetrachlorobenzenes[c]	< 2	5	160	450	200
Pentachlorobenzene[d]	< 2	< 5	< 5	5	30
Combined chlorobenzenes[e]	80	600	1100	600	60

	PCDDs formed (ng/sample)				
Compounds	tetra-	penta-	hexa-	hepta-	octa-
Trichlorobenzenes[b]	30	20	< 5	< 5	< 5
Tetrachlorobenzenes[c]	< 2	5	140	160	30
Pentachlorobenzene[d]	< 2	< 2	< 5	< 5	5
Combined chlorobenzenes[e]	50	220	220	70	5

[a] The reaction was performed in the sealed quartz miniampoules in the presence of air.

[b] 200 μg total with equal amounts of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene

[c] 200 μg total with equal amounts of 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetrachlorobenzene

[d] 200 μg pentachlorobenzene

[e] 500 μg total with equal amounts of all tri-, tetra- and pentachlorobenzenes (7 compounds)

Table 7

Results from pyrolysis of poly (vinyl chloride) (PVC).

PVC-type studied	Process	Product(s)	Yield	Remarks	Ref.
PVC	pyrolysis	Cl-benzenes	ppm range	authors studied only formation of polychlorinated benzenes	19
PVC	combustion on pilot scale on woodchips	Cl-benzenes PCBs	ppm range ppm range	yield of chlorobenzenes increases with increasing temperature	62
PVC	pyrolysis/GC-FID He-gas flow	benzene o-di Cl-benzene	6 % 0,5%	yields increase with increasing temperature	63
PVC chlorinated PVC[a]	pyrolysis 550°C	aromatic (chlor) hydrocarbons		in the case of chlorinated PVC mainly mono- and dichlorobenzenes are formed, max. for 72% Cl-PVC	64
PVC PVC_2^b	pyrolysis	mainly mono-, di- and tri Cl-benzene			65
PVC	pyrolysis	Cl-benzene aromatics, total	1 % 40 %		66

[a] copolymer of vinyl chloride and vinylidene chloride

[b] Poly (vinylidene chloride)

Though most of the PVC is completely destroyed, there is a minor yield of chlorinated aromatic hydrocarbons e.g. chlorobenzenes. For pyrolysis without oxygen this yield is several percent, but in an atmosphere containing oxygen the yield is in the ppm-range.

Most of the authors assume a free-radical chain mechanism (63,64,65). Free macroradicals are indeed demonstrated using ESR techniques (64).

The mechanism implies dehydrochlorination to macroradicals that condense to aromatic products (Reaction 3):

$$\text{PVC} \xrightarrow[-\text{HCl}]{\Delta} \text{free-radicals} \xrightarrow{\Delta} \text{aromatic products} \qquad (3)$$

The yield of chlorinated products is probably the highest in the case of chlorinated PVC, containing over 65% chlorine (non-chlorinated PVC contains 56% chlorine).

Decomposition yields of some aromatics namely benzene, toluene, ethylbenzene, o-xylene, styrene and naphthalene obtained by the pyrolysis of PVC alone at various temperatures are documented in Table 8.

Table 8

Decomposition yields[a] of some aromatics obtained by the pyrolysis[b] of PVC (Geon-103EP) at various temperatures (Reproduced from Iida, Nakanishi and Goto (63)).

	Yield, wt-%					
Product	300°C	400°C	500°C	600°C	700°C	800°C
Benzene	3.50	4.67	5.00	5.23	6.30	9.95
Toluene	-	0.21	0.67	0.82	1.55	2.10
Ethylbenzene	-	-	0.16	0.18	0.18	0.23
o-Xylene	-	-	0.16	0.18	0.23	0.25
Styrene	-	0.13	0.22	0.37	0.74	1.06
Naphthalene	-	0.47	0.52	0.73	1.50	3.00

Table 8 (continued)

[a] Calculated using gas chromatography with p-dichlorobenzene as an internal standard.

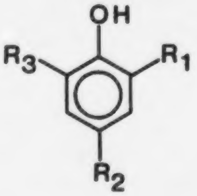
[b] Samples (powder), 1-3 mg, were pyrolyzed in helium gas, flow rate of He bing 25 ml/min.

This table reveals that with increasing temperature, the formation of naphthalene increases in comparison with benzene. In addition, aliphatic hydrocarbons, β-methylnaphthalene, monochlorobenzene, o-dichlorobenzene, p-dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,4-trichlorobenzene were also identified amongst the products of these thermodegradation processes (63).

It is of worth to add that the thermodegradation of a PVC sample always affords benzene as major organic product and hydrogen chloride as main inorganic product (67,68).

Although the thermal degradation of PVC (poly(vinyl chloride)) has been extensively studied, few detailed investigations have been published on the thermal degradation in oxygen. It is, however, generally accepted that the presence of oxygen causes (69): (i) a faster dehydrochlorination, (ii) a less intense discoloration due to shorter polyene sequences, and (iii) chain scission reactions. According to Abbas and Sörvik (69), chain scission mechanisms involving an oxygen attack proceed via β-cleavage of alkoxy radicals; which are formed as a result of interaction of oxygen with the intermediate radical fragment of PVC.

Lignin is an extremely complex polymer. Lignin, which is biosynthesized by plants, occurs in the environment as the second most abundant organic compound (70). Kirsbaum et al. (71) have made investigations on the thermal decomposition of two lignin preparations namely spruce and asp alkaline lignins. The pyrolytic process was performed at the temperature of 475°C. The identified phenolic products during the thermal decomposition of the asp alkaline lignin consist of 26 compounds which include (71): benzaldehyde (3; R = CHO), phenol (3; R = OH), *o*-cresol (4; R = *o*-OH), *p*-cresol (4; R = *p*-OH), *p*-ethylphenol (5), catechol (6), 4-methylcatechol (7), 4-ethylcatechol (8), guaiacol (9), methylguaiacol (10), ethylguaiacol (11), *n*-propylguaiacol (12), vinylguaiacol (13), allylguaiacol (14), *cis*-, and *trans*-isoeugenol (15), vanillin (16), acetovanillin (17), syringol (18), methylsyringol (19), ethylsyringeol (20), *n*-propylsyringeol (21), vinylsyringol (22), allylsyringeol (23), syringaldehyde (24) and monomethyl ether of pyrogallol (25).



5. $R_2 = C_2H_5$, $R_1 = R_3 = H$
6. $R_1 = OH$, $R_2 = R_3 = H$
7. $R_1 = OH$, $R_2 = CH_3$, $R_3 = H$
8. $R_1 = OH$, $R_2 = C_2H_5$, $R_3 = H$
9. $R_1 = OCH_3$, $R_2 = R_3 = H$
10. $R_1 = OCH_3$, $R_2 = CH_3$, $R_3 = H$
11. $R_1 = OCH_3$, $R_2 = C_2H_5$, $R_3 = H$
12. $R_1 = OCH_3$, $R_2 = n\text{-}C_3H_7$, $R_3 = H$
13. $R_1 = OCH_3$, $R_2 = CH = CH_2$, $R_3 = H$
14. $R_1 = OCH_3$, $R_2 = CH_2\text{-}CH = CH_2$, $R_3 = H$
15. $R_1 = OCH_3$, $R_2 = CH = CHCH_3$ (*cis*, *trans*), $R_3 = H$
16. $R_1 = OCH_3$, $R_2 = CHO$, $R_3 = H$
17. $R_1 = OCH_3$, $R_2 = C(CH_3)O$, $R_3 = H$
18. $R_1 = OCH_3$, $R_2 = H$, $R_3 = OCH_3$
19. $R_1 = OCH_3$, $R_2 = CH_3$, $R_3 = OCH_3$

20. $R_1 = OCH_3$, $R_2 = C_2H_5$, $R_3 = OCH_3$
21. $R_1 = OCH_3$, $R_2 = \underline{n}\text{-}C_3H_7$, $R_3 = OCH_3$
22. $R_1 = OCH_3$, $R_2 = CH = CH_2$, $R_3 = OCH_3$
23. $R_1 = OCH_3$, $R_2 = CH_2CH = CH_2$, $R_3 = OCH_3$
24. $R_1 = OCH_3$, $R_2 = CHO$, $R_3 = OCH_3$
25. $R_1 = OCH_3$, $R_2 = H$, $R_3 = OH$

3. THERMOLYSIS IN THE PRESENCE OF INORGANIC CHLORIDES

In the literature, there are few reported instances of the thermal degradation of organic matter in the presence of inorganic chlorides *e.g.* metallic chlorides, during which inorganic chlorine incorporates into organic matter with the resultant production of chlorinated organic compounds. Some pyrolytical reactions of this type as well as reactions involving chlorination processes in the presence of inorganic chlorides are cited below.

Work on chlorination and pyrolysis of Grozen's petroleum coke (particle size ca. 50 μm) in a potassium chloride-sodium chloride melt has been conducted by some Russian research workers (72). Carbon tetrachloride (CCl_4), hexachlorobenzene (C_6Cl_6), hydrogen chloride, phosgene ($COCl_2$), carbon monoxide, carbon dioxide, hydrogen sulfide (H_2S), hydrogen (H_2) and methane were reported as identified products of thermo degradation of petroleum coke in the salt melt.

The quantities of the chlorinated pyrolytic products of the petroleum coke in the salt melt at various temperature (700-1000°C) are recorded in Table 9.

Table 9

Chlorination and pyrolysis[a] of petroleum coke[b] in a potassium chloride-sodium chloride melt[c]. (Reproduced from Shenfel'd et al. (72))

Temperature (°C)	Products (mg/g)			
	CCl_4		C_6Cl_6	
	2h[d]	4h[d]	2h[d]	4h[d]
700	2.0	2.3	0.5	0.7
800	1.5	1.5	0.0	0.0
900	0.1	0.1	0.0	0.0
1000	0.0	0.0	0.0	0.0

Table 9 (continued)

[a] During the process, the helium flow (free of oxygen traces) and dried chlorine (100%) flow were 2 and 7.5 l/hr, respectively. In all the experiments, 80 gm of the melt and 1 gm of petroleum coke were utilyzed.

[b] The composition (wt.%) was: H, 3.51; C, 94.5; ash, 0.5; 0.85; and (O + N), 1.2.

[c] The molecular ratio of the melt was one to one.

[d] Time of pyrolysis.

It is obvious from this Table that chlorocarbons appear in small amounts at lower temperatures and do not appear at raised temperatures (900-1000°C).

According to Shenfel'd et al. (72), the formation of these chlorocarbons is caused by mutual interaction of chlorine with irregular side structure of the coke macromolecules and probably at 900-1000°C the decomposition of the side structures takes place faster than their direct chlorination. Moreover, it is possible that the pyrolysis of the petroleum coke is an initial phase of the process and afterwards the chlorination of pyrolytic products and a binding of chlorine with the coke begin.

Very recently, Mahle and Whiting (73) have subjected bituminous coal to high temperature air oxidation and chlorination using sodium chloride, hydrogen chloride and chlorine gas as a source of chlorine. The purpose of these studies was to determine if polychloro dibenzo-p-dioxins (PCDD's) could be formed by air oxidation and chlorination under controlled small scale laboratory conditions on well characterized coal.

Summary of PCDD's detected after high temperature oxidation and chlorination of coal is documented in Table 10.

Table 10

Polychlorinated dibenzo-p-dioxins (PCDDs) formed by high temperature air oxidation and chlorination of bituminous coal. (Reproduced from Mahle and Whitting (73)).

Experiment		Amount of chlorodioxin species (ppb)[a]			
No.	Material	Tetra	Hexa-	Hepta-	Octa-
I	Coal + Air	ND[b](0.08)	ND(0.1)	0.57(0.3)	1.3(0.7)
II	Coal + Air + NaCl	ND(0.07)	ND(0.2)	0.40(0.24)	2.7(0.5)
III	Coal + Air + HCl	1.40(0.06)	8.40(0.1)	25.00(0.3)	64.00(0.6)
IV	Coal + Air + Cl_2	1.20(0.3)	29.0(0.4)	91.00(2)	290.00(3)

[a] ppb=ng of chlorodioxin/g of coal starting material

[b] ND= not detected; (X.XX)= detection limit

This table indicates that analysis of the reaction of coal with air (Experiment No. 1) and coal, air, and sodium chloride (Experiment No. II) gave apparent positive signals at or near the detection limits for hepta- and octachlorodibenzo-p-dioxin.

Although no real difference between these two experiments was observed, inorganic chlorides in coal have the potential of low level chlorination under certain conditions (73) (discussed below). The oxidation of coal by air bubbling through hydrochloric acid (Experiment No. III) yielded substantial amounts of all analyzed chlorodioxins (see Table 10). These results are significant, because hydrogen chloride is a common component of most pyrolytical processes of chloro organics, as discussed in the preceding Section of the present article. The coal, air, chlorine gas experiment (No. IV) produced the largest amounts of PCDD's of any of the chlorination methods. It should be noted that the data recorded in Table 10 represent the minimum values because the results were not corrected for recovery (73).

In 1809 Gay-Lussac and Thénard (74) reported that silica and sodium chloride react in the presence of water vapour to give hydrochloric acid and sodium silicate. They noted that no reaction occurs at a white heat in the complete absence of moisture, although sodium bromide and iodide at once decomposed under similar conditions. Later on, more extensive investigation on the interaction of sodium chloride with silica was carried out by Clews and Thompson (75). They reaffirmed the findings of Gay-Lussac and Thénard (74). The latter workers (75) concluded that the following reactions (Reactions 4-6) involved:

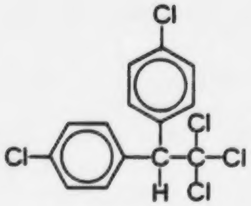
$$4\ x\ NaCl + y\ Si\ O_2 + x\ O_2 \xrightarrow{\Delta} 2\ x\ Na_2O,\ y\ Si\ O_2 + 2\ x\ Cl_2 \qquad (4)$$

$$2\ x\ NaCl + y\ Si\ O_2 + x\ H_2O \xrightarrow{\Delta} x\ Na_2O,\ y\ Si\ O_2 + 2\ x\ HCl \qquad (5)$$

$$4\ HCl + O_2 = 2H_2O + 2Cl_2 \qquad (6)$$

in the interaction of sodium chloride and silica, at the temperatures of 600-1000°C, under various conditions. Reaction 4 occurs in a current of dry air; Reactions 4, 5 and 6 take place in moist air; and Reaction 5 occurs in moist nitrogen. Moreover, in moist air Reaction 5 predominates. Up to 1000°C the magnitude of this reaction is very small and is just discernable at about 600°C. Rise of temperature and increase in the supply of moisture increase the magnitude of the reaction. The evidence for the occurrence of Reaction 6 is provided by the observation that on passing air, charged with hydrogen chloride and water vapour, through a silica tube at 1000°C appreciable quantities of chlorine were formed (75). Of the different varieties of silica investigated, quartz, precipitated silica and tridymite, quartz is the most reactive to sodium chloride at 1000°C. Likewise, Hixson and Tenney (76) noticed that chlorine gas could be formed by the reaction of sodium chloride and sulfur trioxide at temperatures above 330°C.

A few years ago, Chopra and Sherman (77), reported on their investigations into the presence of methyl chloride (CH_3Cl), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) in smokes of tobacco containing varying amounts of 2,2-bis (*p*-chlorophenyl)-1,1,1-trichloroethane (*p*,*p*'-DDT) (*26*).



26

The apparent lack of dependence of the amount of methyl chloride on the quantity of DDT 26 indicated that methyl chloride chlorine comes mainly from tobacco inorganic chlorine. The conclusion of these researchers (77) is also supported by the simultaneous reporting of Johnson and Smith (78) who incorporated inorganic chlorides containing labelled chlorine and found radioactivity in methyl chloride formed in the smoke condensates of cigarettes made from such tobacco (Reaction 7):

$$\text{TOBACCO} + {}^{36}\text{Cl}^- \xrightarrow{\text{smoking}} \text{CH}_3{}^{36}\text{Cl} \qquad (7)$$

Moreover, Chopra and Sherman (77) noticed that there was chloroform in the smoke of tobacco samples containing no p,p̂-DDT (26). However, there was a linear relationship between the amount of 26 and the amount of chloroform found in the tobacco smoke; about 4.6% of the trichloromethyl moiety of DDT in tobacco being converted into chloroform. Such results would indicate that p,p̂-DDT was the only source of $CHCl_3$ in DDT-treated tobacco smoke. Dichloromethane was absent in smoke condensates of untreated and DDT-treated tobacco samples (77).

4. HYPOTHESES ABOUT THERMAL GENERATION OF CHLORINATED DIBENZOFURANS AND DIBENZO-p-DIOXINS IN THE INCINERATORS

The presence of polychlorinated dibenzofurans (PCDF's) and polychlorinated dibenzo-p-dioxins (PCDD's) in fly ash and flue gases of municipal and industrial incinerators can be attributed to three possibilities. It is possible that the tricyclic aromatics namely PCDF's and PCDD's:

. are trace components of refuse and do not undergo an effective thermal destruction,

.. are produced during the combustion and pyrolysis of chlorinated precursors like polychlorinated biphenyls (PCB's), chlorophenols, chlorinated phenoxy acids, polychlorinated diphenyl ethers (PCDPE's) and chlorinated phenoxy-2-phenols,

... are formed as a consequence of a complex array of pyrolytical processes of chemically unrelated organics such as poly(vinyl chloride) (PVC), polystyrene, petroleum coke, coal, tobacco, DDT, chlorocarbons etc. and inorganic chlorine e.g. chloride ions (Cl^-) and hydrochloric acid (HCl); that is to say that these notorious dibenzofurans and dibenzo-p-dioxins are produced via *de novo* syntheses.

No systematic studies have been conducted to prove or rule out the first possibility. These tricyclics could enter the refuse via herbidical formulations, treated wood or products containing PCB's. Analysis of a compost sample, showed PCDF's and PCDD's to be absent from compost. Likewise, in a sample of municipal waste it was demonstrated by Liberty et al. (cited in 22) that no PCDD's were present. Moreover, the extent of contribution of the second possibility (i.e. the formation of PCDF's and PCDD's from the precursors) depends upon the amounts of their precursors present in the wastes and refuses. In order to account for the third possibility (i.e. the formation of these chloropollutants namely PCDF's and PCDD's via *de novo* syntheses) as speculative sources of the chlorinated dioxins and related compounds present in the fly ash and flue gas emissions from the incinerators, we have examined the existing data concerning the pyrolysis of chlorinated and non-chlorinated organic monomers and polymers as well as sodium chloride (NaCl), which have been discussed by us in the preceding sections of the present article. Some speculative thermochemical processes, which according to our opinion are very likely to occur in the municipal and industrial incinerators as well as in the incidental and forest fires, are documented in Fig. 2. This figure indicates the pyrolytical processes involved during *de novo* synthesis of PCDF's and PCDD's from the chemically unrelated organic matter for instance lignins, tobacco, petroleum coke, coal, PVC, PCB's, DDT and chlorocarbons in the presence of O_2 and Cl_2.

Examining the thermal reaction scheme described in Fig. 2, it can be seen that chlorinated and non-chlorinated benzenes and phenols play a key role for the appearance of PCDD's and PCDF's in the municipal and industrial incinerators . Whenever these intermediate compounds are formed in the incinerators, you may ultimately obtain the tricyclic chloropollutants namely PCDF's and PCDD's in the presence of oxygen and chlorine. Reactions like 4 and 6 can be the possible sources of Cl_2 gas required for *de novo* synthesis of dibenzofurans and dioxins. In the structure 27, which represents the thermo degradation products

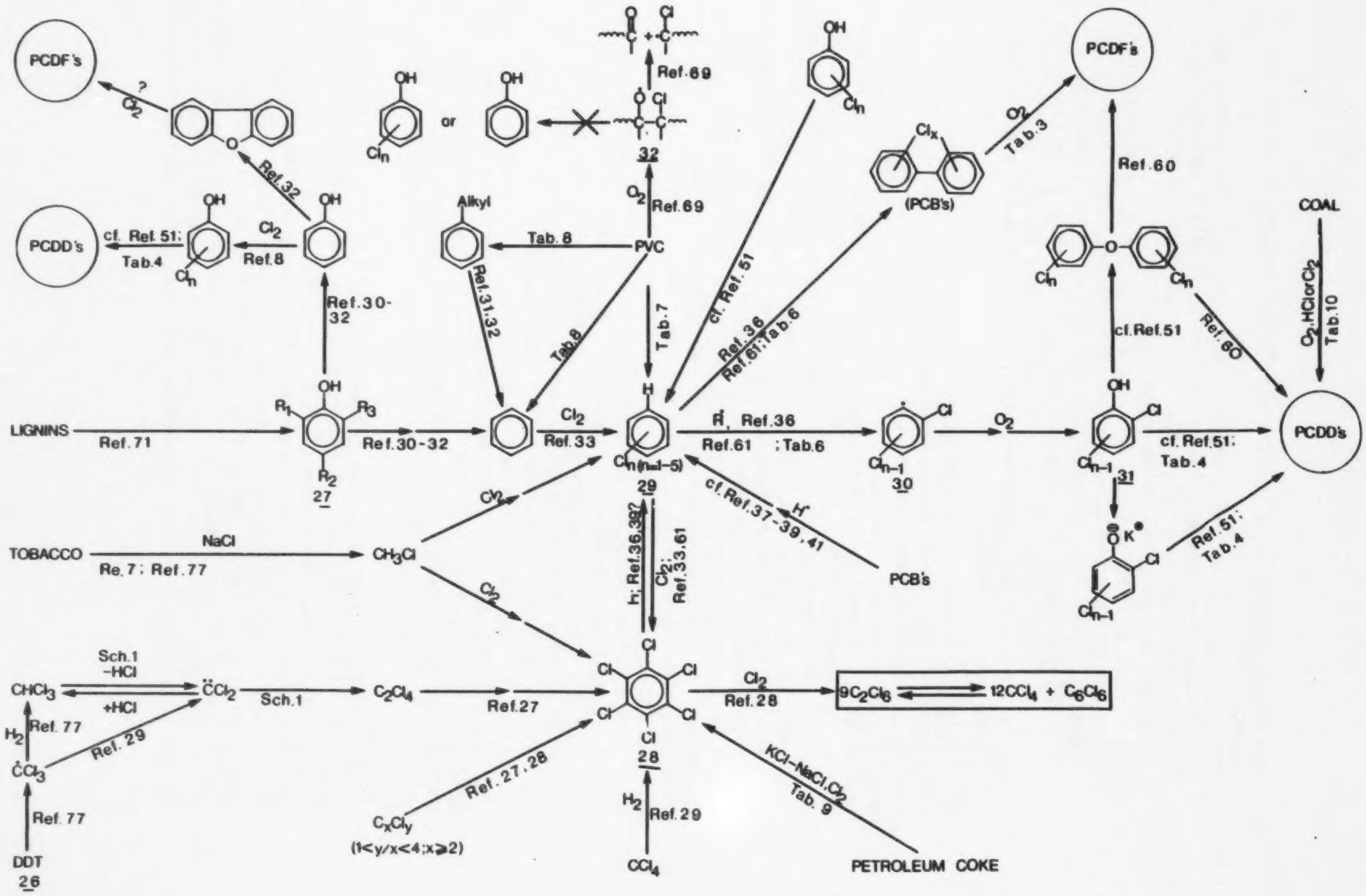

PCDF's
?
Cl2
Ref.32
PCDD's
cf. Ref. 51:
Tab.4
Cl2
Ref.8
Ref.30-
32
OH
Cln
or
Ref.69
32
O2
Ref.69
Alkyl
Tab. 8
PVC
Ref.31.32
Tab.8
Tab.7
cf. Ref. 51
Ref.36
Ref.61; Tab.6
(PCB's)
Clx
O2
Tab.3
PCDF's
Ref.60
COAL
O2,HCl or Cl2
Tab.10
cf.Ref.51
Ref.60
LIGNINS
Ref.71
R1
R2
R3
27
Ref.30-32
Cl2
Ref.33
H
Cln(n=1-5)
29
R, Ref.36
Ref.61 ; Tab.6
Cl
Cln-1
30
O2
31
cf. Ref.51:
Tab.4
PCDD's
TOBACCO
NaCl
Re.7; Ref.77
CH3Cl
Cl2
cf. Ref.37-39,41
H'
PCB's
h; Ref.36,39?
Cl2;
Ref.33,61
O⁻K⁺
Ref.51:
Tab.4
Sch.1
-HCl
+HCl
CHCl3
CCl2
Sch.1
C2Cl4
Ref.27
H2
Ref. 77
Ref. 29
CCl3
Ref. 77
DDT
26
CxCly
(1<y/x<4;x≥2)
Ref. 27,28
Cl2
Ref. 28
9C2Cl6 ⇌ 12CCl4 + C6Cl6
28
H2
Ref.29
CCl4
KCl-NaCl,Cl2
Tab. 9
PETROLEUM COKE

Fig. 2. *De novo* synthesis (a speculative source) of polychlorinated dibenzofurans (PCDF's) and dibenzo-p-dioxins (PCDD's) found in the effluents from the municipal and industrial incinerators. (Re. = Reaction; Ref. = Reference; Sch. = Scheme and Tab. = Table).

of lignins (see Section 2.2), R_1, R_3 is H and/or OCH_3, while R_2 is CH_3 C_2H_5, $n\text{-}C_3H_7$, $-CH = CH_2$,$-CH_2 - CH = CH_2$, $-CH =CHCH_3$, $C^{\nearrow H}_{\searrow O}$ or $C^{\nearrow O}_{\searrow CH_3}$ etc.

Any chlorocarbon, C_xCl_y, which fulfills the following condition:

$$1 < y/x \leq 4; \; x \geq 2,$$

is most likely to generate hexachlorobenzene (28) (27,28). In the presence of chlorine (Cl_2), hexachlorobenzene can be thermally decomposed to perchloroethane (C_2Cl_6) and carbon tetrachloride (CCl_4), and the following equilibrium exists (28),

$$9 \; C_2Cl_6 \rightleftarrows 12 \; CCl_4 + C_6Cl_6 \qquad (1)$$

provided the above mentioned conditions for chlorocarbons are fulfilled. Although, from the literature, we could not find any direct evidence for the reductive dechlorination of hexachlorobenzene, it can be inferred with the support of data described in Ref. 36, 39, that in the incinerators hexachlorobenzene (28) in the presence of H atoms can probably be reduced to chlorinated benzenes 29. The radical species (R· = Alkyl, Cl, H etc.) may attack chlorinated benzenes 29 to abstract hydrogen atoms, whereby *viz.* chlorophenyl radicals 30 bearing *ortho* chlorine substituent are produced (36). The intermediate radical species 30, then react with molecular oxygen to give chlorinated phenols (31) containing *ortho* Cl substituent. The potassim salt of these chlorinated phenols may also provide PCDD's. Finally it should be noted that in the incinerators and other fires, whenever non-chlorinated and chlorinated alkoxide radicals e.g. 32 are formed as a consequence of incorporation of oxygen into the macroradicals (for example see Ref. 69), instead of formation of phenol and polychlorinated phenols, β-cleavage of macroradicals 32 takes place; thereby ketones, aldehydes and alkyl radicals result (69). This observation indicates that, during the thermal formation of PCDF's and PCDD's via *de novo* syntheses from chemically unrelated starting organic material, oxygen always incorporates, when the generation of benzene and chlorinated benzenes has already taken place.

5. FINAL REMARKS

In order to account for the speculative sources of polychlorinated dibenzofurans (PCDF's) and polychlorinated dibenzo-p-dioxins (PCDD's) found in the flue gas and fly ash emitting from the industrial and municipal incinerators, we have considered three possibilities namely: a) PCDF's and PCDD's of the trace levels are already present in the industrial and domestic wastes, b) PCDF's and PCDD's are produced from their precursors during incineration and c) PCDF's and PCDD's are formed in the incinerators through *de novo* synthesis from chemically unrelated organic matter.

For industrial waste all three possibilities have to be considered and the relative contribution of various processes probably depends on the type of waste.

It is evident from Fig. 2 that polychlorinated benzenes and polychlorinated phenols are key intermediate compounds of prime importance in *de novo* syntheses of PCDF's and PCDD's from any starting organic matter. Mechanisms of the incorporation of inorganic chlorine into organic matter as well as further discussions on this topic with the support of additional data will be presented somewhere else.

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PARTICULATE AND VAPOR PHASE EMISSIONS OF CHLORINATED DIOXINS FROM COMBUSTION SOURCES

J. C. HARRIS and C. E. RECHSTEINER
Arthur D. Little, Inc.
Cambridge, MA

ABSTRACT

Data on polychlorinated dibenzo-p-dioxins in effluents from full scale combustion sources will be discussed, with emphasis on the distribution of these species between particulate and vapor phase emissions. The implications of this distribution on the effectiveness of both sampling procedures and possible emission control strategies will be discussed.

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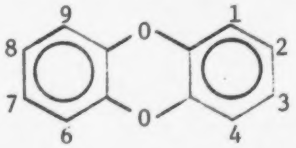
INTRODUCTION

Recent discussions in the public press and in the scientific literature have led to awareness in both the scientific and the lay communities of potential harmful effects associated with human exposure to organic chemicals in the environment. Among the chemicals that have received considerable attention are the dioxins (more formally, the polychlorodibenzo-p-dioxins), including the particular compound 2,3,7,8-tetrachlorodibenzo-p-dioxin, which occur as trace (part per million) contaminants in a variety of polychlorophenol-based chemical products. It has been reported that the dioxins are also present, at (part per trillion) levels, in effluents from combustion sources such as incinerators. (1,2,3)

The polychlorinated dibenzo-p-dioxins (PCDDS) are organic chemical compounds which share the basic molecular structure of the dibenzo-p-dioxin nucleus, below, and contain one to eight chlorine atoms located at any of the eight positions on the two aromatic ring portions of the molecule. The possible chlorine substituent positions are numbered as shown below.



Polychlorinated dibenzo-p-dioxins may exist in several isomeric forms. Isomers are compounds that have the same molecular formula, but different patterns of substitution or molecular geometry. In the case of the PCDDs, the possible permutations of one to eight chlorine atoms give rise to a total of 75 possible isomers, each of which will possess distinct physical, chemical, and biological properties. Figure 1 shows a number of examples.

PCDDs are not manufactured commercially as intended products, except possibly in small quantities for research. However, these species can be formed inadvertently as trace contaminants in the manufacture of industrial chemicals, such as polychlorophenols and related products. The PCDD contaminant produced in the case of 2,4,5-trichlorophenol is predominantly 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). This PCDD isomer has been the most thoroughly studied and, indeed, is the only isomer for which an extensive data base on toxicology and environmental fate exists. The focus on 2,3,7,8-TCDD reflects both its presence in the commercial formulations derived from 2,4,5-trichlorophenol, which have had rather widespread use, and its exceptionally high toxicity.

Table 1 indicates some basic physical chemical properties of 2,3,7,8-TCDD. The low water solubility, low vapor pressure and high octanol:water partition coefficient serve as indications that this compound has the potential to adsorb and remain bound to solid surfaces

PCDD	Total # of Isomers
Dichloro-dibenzo-p-dioxin	10
Trichloro-dibenzo-p-dioxin	14
Tetrachloro-dibenzo-p-dioxin	22
Pentachloro-dibenzo-p-dioxin	14
Hexachloro-dibenzo-p-dioxin	10
Heptachloro-dibenzo-p-dioxin	2
Octachloro-dibenzo-p-dioxin	1

Example Structures

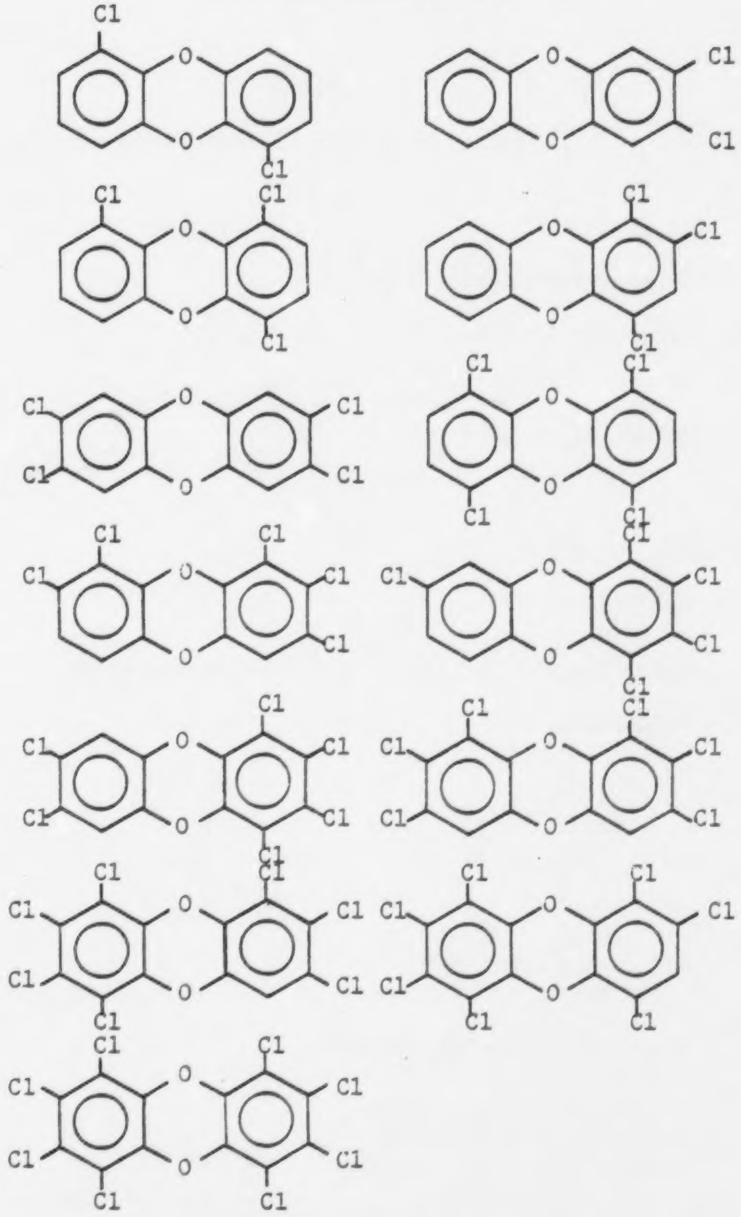
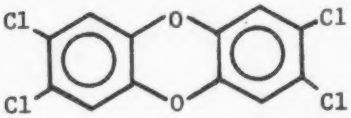


Figure 1. Example Structures of PCDD Isomers

TABLE 1

Physical and Chemical Properties of TCDD

	Parameters
Molecular weight	322
Molecular formula	$C_{12}H_4Cl_4O_2$
Molecular structure	
Boiling point	-
Melting point	303-305°C
Vapor pressure	Estimated to be 10^{-6} - 10^{-7} mm Hg
Solubility	
water	0.0002 mg/L
benzene	57 mg/L
n-octanol	4.8 mg/L
methanol	1.0 mg/L
Log octanol:water partition coefficient	7.14 (calculated)
Chemical Abstracts Service No.	1746-01-G
NIOSH Toxic Substances List No.	HP 35000

Source: Reference 1

with which it comes in contact. 2,3,7,8-TCDD might therefore be expected to be associated primarily with the particulate phase material in atmospheric emissions. However, the equilibrium saturated vapor concentration corresponding to the estimated 10^{-6} to 10^{-7} mm Hg vapor pressure is 2-20 $\mu g/m^3$; 2,3,7,8-TCDD may be present in the vapor phase at concentrations below this level.

It can be expected that di- and trichloro-PCDDs will have higher vapor pressures and water solubilities but lower octanol:water partition coefficients than does TCDD. Conversely, PCDDs with a higher degree of chlorination, such as octachloro-CDD, will have lower vapor pressures and water solubilities and higher octanol:water partition coefficients than does TCDD.

SAMPLING PROCEDURES

The sampling procedures developed for testing of combustion sources, such as municipal and industrial waste incinerators, is crucial to the success of the test in terms of obtaining accurate measurements. It is important to collect a sample which is as representative as possible of the actual effluent concern. This is determined by the choice of the number and size of samples collected and the location of sampling points, as much as by the details of the actual sampling technique. The selection of an appropriate sampling system to ensure collection of all physical forms of the flue gas components is also important.

From an incinerator, several forms of effluent may be sampled: stack gas, fly ash, bottom ash and/or scrubber water. Of these effluents, the stack gas with its entrained particulate is of greatest importance for the determination of PCDDs since these streams lead directly to emissions of PCDDs into the atmospheric environment. The only truly reliable method of determining the levels of PCDDs in the combustion facility stack gas effluent appears to be collection of the integrated samples of flue gas from the stack gas itself. Measurements of PCDDs in other types of samples, such as fly ash from an electrostatic precipitator or other device upstream of the stack, can only be indicative, not definitive of actual PCDD emissions. To identify and quantify potential flue gas emissions, it is necessary to use a stack sampling system capable of collecting both particulate and vapor phase organics. The state of the art for this purpose is a comprehensive sampling train that incorporates cyclone/filter components for particulate collection and a trap filled with solid sorbent for collection of organic vapors. Two such trains which have been used in the field are the modified Method 5 train (4) and the Source Assessment Sampling System (SASS) (5,6).

The standard EPA Method 5 sampling train, modified (Figure 2) to incorporate a sorbent module containing florisil or XAD-2, has been widely used for sampling combustion source effluents. This train is based on a Federal Register procedure and has been used to sample flue

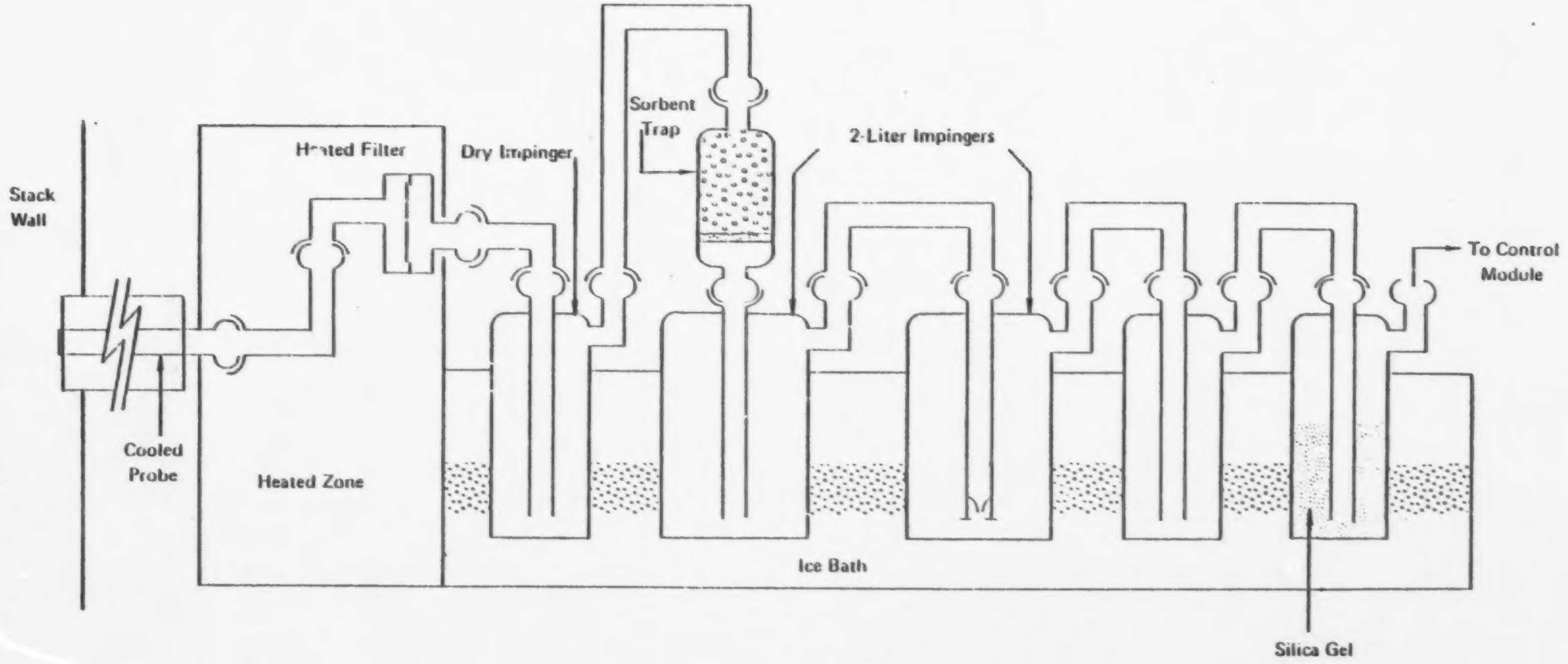

Stack Wall
Cooled Probe
Heated Filter
Heated Zone
Dry Impinger
Sorbent Trap
2-Liter Impingers
To Control Module
Ice Bath
Silica Gel

Figure 2. Method 5 Train Modified for Collection of Organic Vapors

Source: Reference 1.

gases from the combustion zones of commercial scale incinerators in a field study of thermal destruction of hazardous waste (1). Two other features of the Method 5 train are its compatibility with traversing of the stack and the isokinetic sampling. One drawback to this train for PCDD determination is its relatively low sample flow rate of about 3/4 to 1 cfm. During a normal sampling session of 3-4 hours, the amount of stack gas sampled would be about 5 m^3. Using an analytical method with a detection limit corresponding to a concentration of 50 pg/μL and appropriate extraction, clean-up and concentration procedures, a 5 m^3 sample would give a minimum detectable source level of approximately 1 part per trillion. The quantity of PCDDs in the sample prior to extraction would be 5 ng (10^{-9} g).

The Source Assessment Sampling System (SASS) (Figure 3) was designed and is made by Acurex for EPA Process Measurements Branch, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. It is essentially a fivefold scale-up of a Method 5 including cyclones for size separation of particulates and a sorbent trap (2,3). The main advantage is the larger sample size achievable by virtue of the higher sample flow rate. Disadvantages are that it is too big for traversing the stack and that the cyclones are not compatible with true isokinetic sampling (varying sample flow rate changes the cyclone cutoffs). The stack gas sampling rate of a SASS train is about 4 cfm which translates to a 30 m^3 sample if collected continuously for four hours. The detection limit achievable with the SASS train is thus about 5 times lower than that for the modified Method 5, or about 0.2 ppt.

A sampling protocol must also designate the number of samples to be collected at any facility. In general, multiple samples, each integrated over a reasonably long period of time (hours), must be collected to make possible an accurate representation of the effluent stream from the tested facility. A single sample collected for later PCDD determination gives no indication of the precision of the measurement. Although two samples would allow an average level of PCDD to be determined, at least three samples must be analyzed in order to compute an error bound for the measured values. Acquisition of more than three samples from a given effluent stream may improve the precision of any measurements but may not be cost effective in terms of the additional precision. In general, three complete stack sampling runs is the minimum number that would allow a rough estimate of precision to be made.

ANALYTICAL PROCEDURES

Methodology for analysis of PCDDs, especially 2,3,7,8-TCDD, has been reviewed in some detail elsewhere (1,2,3.7) and will be discussed only briefly here.

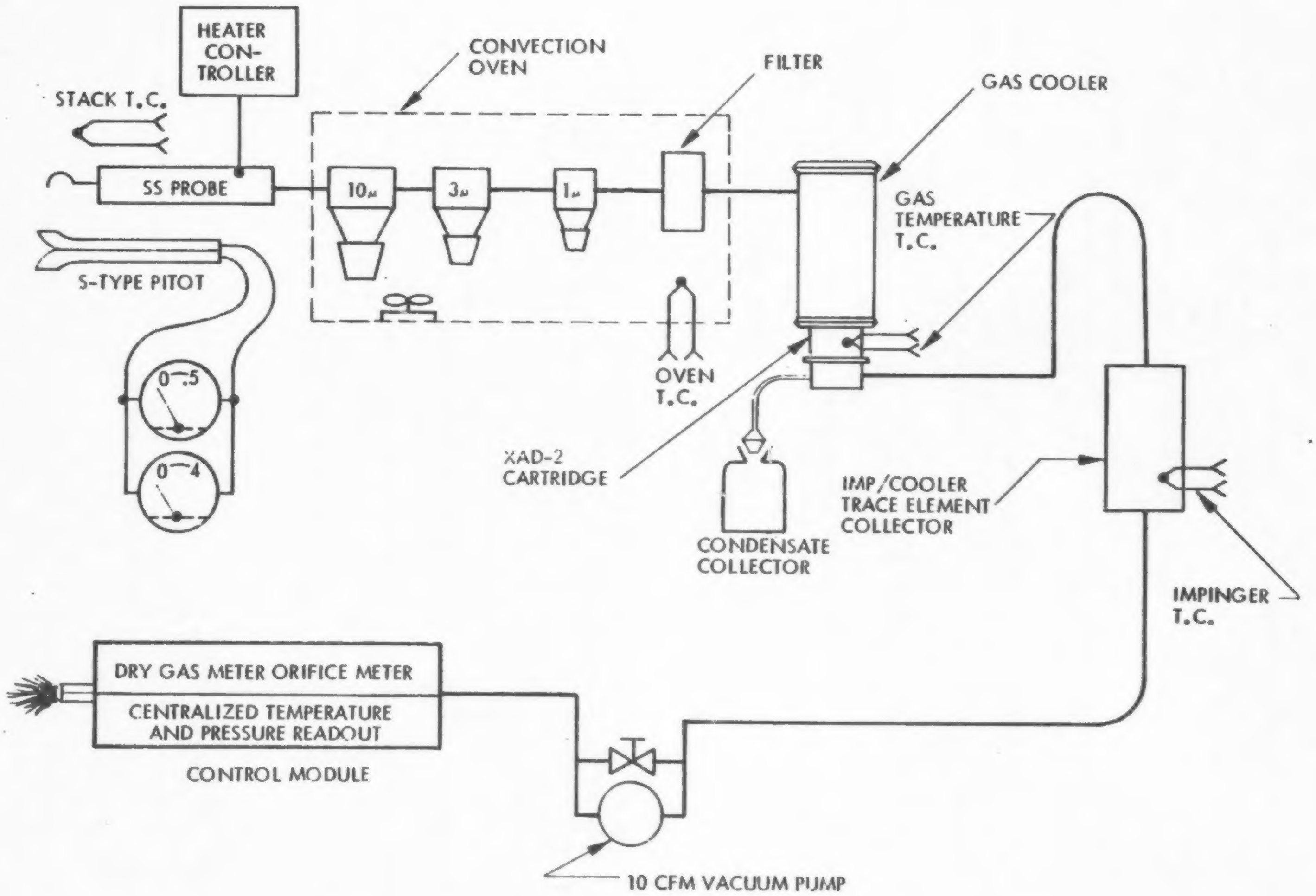

HEATER CON- TROLLER
CONVECTION OVEN
FILTER
GAS COOLER
STACK T.C.
SS PROBE
10μ
3μ
1μ
GAS TEMPERATURE T.C.
S-TYPE PITOT
0-.5
0-4
OVEN T.C.
XAD-2 CARTRIDGE
CONDENSATE COLLECTOR
IMP/COOLER TRACE ELEMENT COLLECTOR
IMPINGER T.C.
DRY GAS METER ORIFICE METER
CENTRALIZED TEMPERATURE AND PRESSURE READOUT
CONTROL MODULE
10 CFM VACUUM PUMP

Figure 3. Source Assessment Sampling Schematic

Source: EPA 600/2-76-160a, June 1976 p.30

The preparation of environmental samples for PCDD analysis involves two major steps, the extraction of the sample and clean-up of the sample extract. In many respects, the extraction and clean-up of the sample are the most critical steps of the analysis procedure. The detection limits for PCDDs in samples of environmental concern are in the low parts per trillion range (1 part per trillion is equivalent to 1 part in 10^{12}) which requires that the sample extraction and clean-up steps separate PCDDs from the bulk of the sample material. The amount of the non-PCDD material removed must be in excess of 99.99%. Further, several common environmental contaminants which have similar chemical behavior, i.e., the pesticides DDE and DDT and the Aroclor series of polychlorinated biphenyls (PCBs) must also be separated from PCDDs for successful measurement of PCDD. Thus, the sample extraction and clean-up steps not only need to isolate PCDD from a majority of the sample matrix, but also need to separate PCDD from chemicals which behave similarly in many ways and are also typically present at much higher levels than parts per trillion.

The methods currently in use for sample extraction and clean-up for analysis of 2,3,7,8-TCDD include Soxhlet or ultrasonic extraction with benzene, toluene or other organic solvent. A hot, caustic reflux of the sample is used for some matrices (biological tissues). Several methods for clean-up of the sample extracts to remove, or at least minimize, the levels of interfering compounds are available. Most of the methods use a series of conventional column chromatography steps, although one method which uses high performance liquid chromatography has also been described (3) for 2,3,7,8-TCDD. Equivalent procedures would be required to achieve the same degree of specific identification and quantification of any other PCDD isomer.

The method of choice for the analysis of 2,3,7,8-TCDD is combined gas chromatography-mass spectrometry (GC/MS) (6,7,8). This technique has the sensitivity and specificity to perform 2,3,7,8-TCDD analysis in the parts per trillion range provided there has been suitable sample preparation beforehand. The GC portion of the system has as its function the separation of the prepared sample into discrete components (which may not be perfectly separated from one another) while the MS portion of the system has as its function the detection of, identification of, and quantification of the compound(s) of interest, such as 2,3,7,8-TCDD.

The GC portion of a GC/MS system separates a complex sample into a number of discrete peaks resolved in time from one another which contain from one to several components. The degree of resolution achieved is largely a function of the type of column used for analysis. A packed column, containing a coated substrate, typically gives fairly low resolution which may nevertheless be more than adequate for PCDD class separations and determination of total TCDDs, etc. High resolution on capillary column GC, in which the GC phase is coated onto the wall of a long, narrow diameter column, is being extensively used for 2,3,7,8-TCDD determination for several reasons. Capillary GC columns reduce the number of components found in any single resolved GC peak as compared to packed column GC. This reduces the possibility of interferences from co-elution of other compounds. The higher resolution of capillary GC columns also permits the separation of closely related isomers, e.g., 1,2,3,4-TCDD and 2,3,7,8-TCDD may be completely resolved on capillary GC columns which may not be the case for packed GC columns. Additionally, the sharp peaks produced with capillary GC columns increase the signal-to-noise ratio for each component compared to that with packed GC columns which affects the detection limit for any component.

Packed GC columns are best suited to chlorinated dibenzo-p-dioxin class determinations and for screening of samples for PCDDs where the high resolution of capillary columns is not needed. For class determination, the separation of the individual tetrachloro isomers is of less importance than the separation of tetrachloro isomers from penta- and hexachloro isomers. For sample screening, a small number of false positives are preferred over any number of false negatives. For these two examples, the use of packed columns may be preferred to extend the life of the capillary columns which are used for specific isomer determinations.

The MS portion of a GC/MS system provides the specificity and sensitivity needed for low level analyses. In a mass spectrometer, the components of a sample are ionized and the ions formed are detected as a function of their mass. The mass spectrum of a compound, the pattern of the intensities of the ions formed at all mass-to-charge (m/z) ratios, is unique except for closely related structural isomers (e.g., 1,2,3,4-TCDD and 2,3,7,8-TCDD will have very similar mass spectra). Hence, compound identification may be made based on the mass spectrum. The m/z of any ion formed is determined by the masses of the atoms actually contained in each molecule or fragment ion and the charge of the ion.

Two types of mass spectrometers are available for TCDD analyses; low resolution instruments (LRMS) and high resolution instruments (HRMS). A low resolution MS (LRMS) measures ions to the nearest whole m/z unit (e.g., both m/z 319.8 and 320.2 are detected at m/z 320). If ions of m/z 319.8 and 320.2 were present at the same time in the mass spectrometer, their individual signals would add together to form an intensity at mass 320. To differentiate between two compounds, each of which has one of these ions in its spectrum, more than one specific m/z value, and perhaps the entire mass spectrum, would need to be examined. When analysis of low levels of organics is involved, multiple ion detection, with or without signal averaging, is required to achieve adequate specificity and sensitivity.

A high resolution instrument is advantageous for use in PCDD analyses for two reasons. HRMS techniques measure accurate masses for sample ions while simultaneously separating multiple mass spectral peaks which occur at the same integral m/z value. Thus, the high resolution mass spectrometer may be adjusted to measure the specific mass-to-charge ratios required for identification of a selected PCDD (such as tetra, penta, hexa, etc.) while eliminating those interferences which may have ions at the same nominal mass-to-charge ratio as those for the PCDD compound(s) of interest but are sufficiently different in exact m/z ratio to be resolved by the HRMS. For example, HRMS would allow discrimination between an ion formed from TCDD (with atomic composition $C_{12}H_4O_2{}^{35}Cl_4$) at m/z 319.8965 and one formed from an interference (with atomic composition $C_{14}H_8{}^{35}Cl_2{}^{37}Cl_2$) at m/z 319.9318.

The choice of using LRMS or HRMS depends on the goal of the analysis and the analytical cost. LRMS is less expensive than HRMS, both in terms of initial instrument purchase price and routine upkeep costs. As a screening technique, LRMS is well suited. While LRMS permits some false positives to be tagged for further work, it allows no false negatives. For a determination of total TCDD in a sample, i.e., 2,3,7,8-TCDD and the other tetrachloro isomers, either LRMS or HRMS may be used with the analysis cost of LRMS being about one-half that of HRMS. For a specific 2,3,7,8-TCDD determination, capillary column GC with HRMS is a necessity to separate the 2,3,7,8 isomer from other isomers and to insure that the sample does not show any interferences.

Table 2 is offered as one method of comparing the analysis methods for 2,3,7,8-TCDD analysis in terms of cost, sensitivity and applicability. For a typical study using the approximate costs found in Table 2, with an analysis protocol of blank, sample, blank, spiked sample, blank, using caustic digestion, two column clean-up steps, and HRGC/HRMS, the approximate costs would be $2,000-6,000 per actual unknown sample. This type of analysis protocol is common for measurements of 2,3,7,8-TCDD which require detection limits in the low parts per trillion. The analysis of blanks and spiked samples helps to assure that any TCDD found in a sample is not an artifact of the analysis procedure, e.g., TCDD-contaminated glassware, etc., but is contained in the sample. When deciding upon the procedure to be used for a specific program, the goals of the program must be considered and the method chosen must satisfy these goals.

EMISSION OF DIOXINS FROM COMBUSTION PROCESSES

Production of PCDDs from pyrolysis or combustion of chlorinated aromatic species has been demonstrated in several laboratory scale experiments (2,3,8,11). Chlorinated phenols have been found to be the best PCDD precursors; polychlorobenzenes and polychlorobiphenyls have also been found to give detectable yields of PCDDs. The results of the laboratory studies and their implications regarding detailed mechanisms of PCDD information have been discussed elsewhere (7).

Within the past three years, there have been several reports of the detection of dioxins, and specifically tetrachlorodibenzo-p-dioxins (TCDDs), in emissions from full-scale combustion facilities. An

TABLE 2

COMPARISON OF METHODS FOR TCDD/PCDD ANALYSIS

Method	Approximate Time	Approximate* Cost/Sample ($)	Limit of Detection	USE: PCDD Cl Containing Group	USE: Specific PCDD Isomer	USE: Screening	Comments
a) Sample Extraction							
Caustic Digestion	1-2 days	480-960	--		✓		Reported to lose higher chlorinated dioxins with caustic reflux.
Neutral Extraction	1/2-1 day	240-480	--	✓	✓		EPA method not validated.
b) Sample Clean-up							
Column Chromatography	1/2-1 da.	240-480	--	✓	✓		Primarily alumina, often 2 columns used sequentially. Also silica and florisil and combinations of the three.
HPLC	6 hr	200	(100 ppb)	✓		✓	Can be used quantitatively as screening method used by Dow as final clean-up step.
c) Analysis							
LRGC/LRMS	6 hr	600-1000	10-50 ppt	✓		✓	Always use multiple ion detection (MID) for detection.
HRGC/LRMS	6 hr	1000-1500	8 ppt		✓		Always use multiple ion detection (MID) for detection.
LRGC/HRMS	6 hr	1000-1500	4-5 ppt	✓		✓	Always use multiple ion detection (MID) for detection.
HRGC/HRMS	6 hr	1500-2000	2-50 ppq		✓		Always use multiple ion detection (MID) for detection.
NCI	--	--	2 pg		✓		Experimental stages, procedures incomplete and need development.
IKE/MIKE	--	--	500 pg				Experimental stages, procedures incomplete and need development.

*Cost per sample assuming single determination on sample itself, plus one blank and one standard per sample. Cost for screening and verification within a factor of 2. Cost for blanks should be less than for real samples.

annotated listing of these observations is presented in Reference 1. That list includes:

Municipal Incinerators

The Netherlands
Switzerland
Germany
Canada
Japan
United States

Industrial Waste Incinerators

Switzerland
United States

Hazardous Waste Incinerators

At Sea

Oil/Coal-Fired Powerhouse

United States

Miscellaneous Sources.

More recently, data for additional municipal waste incinerators (2,12) and for hazardous waste incinerators destroying polychlorinated biphenyls (PCBs) (13,14) have been reported.

The results published by Buser and Bosshardt (15) for a municipal incinerator in Switzerland illustrate the type of information that is available from the reported studies.

Fly ash from the electrostatic precipitator at the Zurich-Hagenholtz incinerator, which burns municipal/industrial refuse but no known chemical waste, was analyzed. A two-stage column clean-up procedure and capillary GC/MS were used to obtain the following quantitative data on PCDDs in the fly ash:

octachloro - 120 ng/g (ppb)
heptachloro - 60 ng/g
hexachloro - 30 ng/g
pentachloro - 8 ng/g
tetrachloro - 2 ng/g

The GC/MS analysis indicated the presence of multiple isomers of tetra- through hepta-CDDs.

In a subsequent study (16), Buser _et al_. investigated the specific isomers present in the extracts from this fly ash sample. At least 12 different TCDD isomers/isomer clusters (theoretical maximum of 22 isomers) could be identified. The principal species were 1,3,6,8- and 1,3,7,9-tetrachlorodibenzo-p-dioxins, which would be the expected condensation products from a 2,4,6-trichlorophenol precursor. The peak whose retention time corresponds to that of the especially toxic 2,3,7,8-isomer is a relatively minor component (16). Buser _et al_. consider the similarity between the isomer distributions ("fingerprints") observed for the fly ash sample and for the product of laboratory-scale pyrolysis of a mixture of commercial chlorophenols to be remarkable, although the patterns are not identical. This observation is consistent with, but does not prove, the hypothesis that commercial chlorophenols in the municipal/industrial refuse might be the precursors of the PCDDs in the incinerator effluent.

An estimate of the stack emissions of PCDDs that might be associated with a municipal waste incinerator such as that studied by Buser and Bosshardt can be derived by assuming that the stack fly ash has approximately the same composition as that collected in the electrostatic precipitator hopper. Knowledge of the control device efficiency would then allow calculation of atmospheric emissions of particulate PCDDs. Lacking the specific data on efficiency of the particular control device, one can calculate the stack concentration of PCDDs that would correspond to the United States Environmental Protection Agency New Source Performance Standards for particulate emissions from incinerators: 0.08 gr/SCF or 180 mg/m^3. At this particulate loading, the fly ash PCDD concentrations reported by Buser and Bosshardt would correspond to stack concentrations of 40 ng/m^3 of total PCDD (tetra- through octa-CDDs) and 0.4 ng/m^3 of all TCDD isomers combined. The 2,3,7,8-TCDD would, according to Buser _et al_., be no more than a fraction of the 0.4 ng/m^3.

Based on data for this and other municipal waste incineration facilities, including the data summarized by Hutzinger and co-workers (2), Arthur D. Little, Inc. has estimated (19) emission factors (lbs of PCDD/ton of municipal refuse) of about 4.8 x 10^{-6} for total PCDDs (tetra- through octa-CDD), 3.5 x 10^{-7} for TCDDs (all isomers combined) and 3.5 x 10^{-8} for 2,3,7,8-TCDD. For a specific 60 ton/hour, 170,000 DSCFM proposed municipal waste incineration facility, these emission factors correspond to estimated ground level ambient concentrations, on an annual average basis, of about 1-3 pg/m^3 for total PCDDs, 0.07-0.2 pg/m^3 for TCDDs (all isomers combined) and 0.007-0.020 pg/m^3 for 2,3,7,8-TCDDs (19). Stack concentrations would be on the order of 10^4 times higher than these estimated ambient levels, or about 10-30 ng/m^3 of total PCDDs, 0.7-2 ng/m^3 of TCDDs, and 0.07-0.2 ng/m^3 of 2,3,7,8-TCDD.

For comparison, EPA measurements of TCDD from hazardous waste incinerators burning polychlorinated biphenyls indicated stack emission levels of 0.18 ng/m^3 of TCDDs (all isomers combined) from an El Dorado, Arkansas facility (13) and 0.64 ng/m^3 of TCDDs (all isomers combined) from a Deer Park Texas facility (14). Maximum ambient ground level concentrations on the order of 1-10 pg/m^3 of TCDDs (all isomers combined) were predicted (13,14).

INTERPRETATION

The existing data base on emissions of PCDDs from combustion sources is too small to allow general conclusions to be drawn with confidence. Most of the observations to date result from qualitative and/or quantitative analysis of a single sample per facility, which is at best representative of the emission from that source at one point in time. The few publications that have reported results of multiple sampling runs at a particular facility have indicated variations as large as two orders of magnitude in quantitative PCDD levels (3) and also inversions in the qualitative order of abundance of the polychlorinated organic species in the effluents (17). This degree of variability is not especially surprising for facilities burning such heterogeneous feedstocks as municipal or industrial waste. It is, however, sufficient reason for exercising caution in attempting to compare emission data for one facility at one time with those for another time or another facility (even one of the same generic type).

Most published reports have focused on PCDDs in particulate fractions (fly ash) of combustion effluents, particularly fly ash recovered from electrostatic precipitator (ESP) control devices at incinerator facilities. This focus may be atrributed to several factors. First, particulate emissions are part of the "classical" pollutant set (NO_x, SO_x, and "rocks") that has historically received greatest attention and has been addressed by government standard setting. Second, and more importantly, it is known (24,25) that organic materials, such as PCDDs, are adsorbed onto particulate material and are associated with the particulate fractions of ambient air samples. Third, and by no means least, is the fact that sampling of fly ash from the hopper of an ESP is much less difficult than extractive sampling of particulate plus vapor components of the flue gas. Notwithstanding all of these factors, the focus on ESP fly ash may not be sufficient for complete evaluation of the potential PCDD emissions. An ESP is relatively more effective for removal of large particles than of small (sub-micron) particles, which are, therefore, most abundant in the flue gas emitted from the stack. The sub-micron particulate is frequently a minor (<1%) contributor) in terms of the total mass of particulate emitted in an uncontrolled incinerator effluent, but it typically shows a much higher concentration of adsorbed organic pollutants than does the larger diameter particulate material (18).

The possiblity of vapor vs. particulate-bound emissions of PCDDs must be considered. It is quite possible that PCDDs exist partly in the vapor phase when present in low concentration at stack temperatures. A species with an equilibrium vapor pressure of about 10^{-8} mm (lower than that estimated for TCDD at ambient temperature) would have a saturated vapor concentration of 100 ppt (v/v) in air. The vapor pressure, and hence the fraction of the TCDD possibly present in the vapor phase vs. adsorbed on particulate, will be lowest for octachlorodibenzodioxins and higher for the less chlorinated species. Variations in vapor phase concentration as a function of temperature may be responsible for part of the variation in PCDD group distributions from different facilities. An ESP which ran hotter would tend to have a higher ratio of octachloro to tetrachlorodibenzodioxin in the collected fly ash, all other things being equal. Flue gas sampling with a comprehensive sampling train and separate analysis of the particulate (cyclon/filter) and vapor (solid sorbent/impinger) components will be necessary to resolve this question. The data reported by Cavallaro et al (12) for four municipal waste incinerators in Italy suggest that vapor phase emissions of TCDD may be 2-10 times higher than particulate phase emissions in stack gas from these facilities.

POTENTIAL CONTROL OF EMISSIONS

Technology for emission control must usually be discussed in the context of criteria which define the degree of control required, such as those established by effluent guidelines, air quality criteria, or new source performance standards. Such criteria have not yet been established for PCDDs (or for other specific organic chemicals or classes) in combustion source effluents.

The state of the art of pollution control devices does not encompass technology for specific removal of part-per-trillion levels of organic pollutants in flue gas. It may be necessary to consider control of both particulate and vapor phase emissions. There appear to be three generic approaches to potential control of PCDD or dioxin emissions. To the extent that PCDDs in combustion source effluents are associated with particulates, state-of-the-art particulate control technology can achieve a reduction in PCDD emissions to the ambient air. Alternatives to particulate removal as approaches to PCDD control can be identified generically, if not specifically. They are basically: identify and eliminate PCDD precursors in the combustion source influent and modify combustion conditions to minimize formation of and maximize destruction of PCDDs.

Control of Particulate Emissions

Most of the reported PCDD "emissions" from combustion sources have been based on measurements of PCDD in fly ash removed from the effluent stream by particulate pollution control devices. The degree of PCDD reduction that can be accomplished by removal of particulate from the flue gas will depend, as noted earlier in this report, on the size distribution of the particles to which the PCDDs are adsorbed. The one preliminary piece of experimental evidence that speaks to this point (13) suggests that a considerable fraction of the PCDD may be associated with sub-micron particles; state-of-the-art particulate control devices are most efficient for removal of larger particles. The data base at present is too limited to allow reasonable inferences to be drawn on the all-important quantitative aspects of the effectiveness of particulate removal for PCDD emission control. It can be foreseen, however, that disposal of fly ash collected from an electrostatic precipitator or of spent scrubber water from a wet scrubber will be an important and non-trivial issue to be addressed in considering this approach to PCDD emission control.

Identification/Elimination of PCDD Precursors

Identification and elimination of PCDD precursors in the combustion source influents may be feasible if and only if there are a relatively small number of organic chemicals that function as precursors. If every chlorinated organic compound is regarded as a potential precursor, then control of precursors in municipal waste incinerator influents would appear impossible. The range of possible precursors for formation of detectable quantities of PCDDs is probably not that broad, since even "good" PCDD precursors, such as polychlorophenols and polychlorobenzenes, show very low PCDD converison efficiencies. However, the chlorophenols and chlorobenzenes are quite widely distributed as components of a variety of products, including consumer products such as weed killers, wood preservatives, moth balls, etc. The only practical way to eliminate all potential sources of these materials in municipal waste would be to ban their use. On the other hand, it may be possible to eliminate only one or a few of the present major uses of the suspect principal precursor(s) and achieve a substantial degree of PCDD reduction. In summary, evaluation of the feasibility of this approach to PCDD emission control will require data on the number and kinds of probable PCDD precursors in influents, plus materials balance (production and use) analysis of those chemicals suspected to be most important as precursors.

Modification of Combustion Conditions

Modification of combustion conditions to minimize PCDD formation and maximize PCDD destruction is another alternative approach. Most large scale combustion facilities, including both municipal and industrail waste incinerators, are designed to operate at nominal combustion zone temperatures in excess of the 800°C (1470°F) that has been cited (1) as necessary for destruction of TCDD. On the other hand, many municipal waste incinerators are not designed to fulfill the more stringent combustion criteria ordinarily recommended for incineration of hazardous or thermally stable organic species (3,31).

Process parameters that influence overall combustion efficiency and might, therefore, be expected to have a significant impact on PCDD levels in combustion effluents are:

- temperature in the combustion zone,
- residence time within the combustion zone,
- air to fuel ratio, and
- turbulence or mixing efficiency.

A detailed discussion of the importance, effects and interdependent nature of these parameters is beyond the scope of this report. It may be noted, however, that process parameters for an existing combustion facility can normally be varied from the design parameters only within a fairly restricted operating range. In a field investigation of the destruction of chemical wastes in commercial scale incinerators (31), it was found that combustion/destruction efficiencies were independent of adjustable process parameters (temperature, residence time, fuel feed rate) over the accessible range for each facility tested. Facility modifications to achieve more substantial changes in process parameters may be technically feasible in some instances, but not in others.

CONCLUSIONS

Measurement of Dioxins in Combustion Process Effluents

- State-of-the-art methodology for sampling requires collection of replicate, time-averaged samples of stack gas effluent. A comprehensive sampling train is needed for collection of both particulate and vapor phase material.

- Sample preparation and clean-up are critical steps in the analysis procedure for PCDDs to achieve low detection limits and eliminate false positive results from interfering chemicals.

- Gas chromatography/mass spectrometry represents the state of the art for analysis of total PCDDs and/or specific PCDD isomers. Low resolution procedures are useful for screening; high resolution techniques are necessary for reliable confirmation of apparent positive identifications. Detection limits on the order of pg of PCDDs per g of particulate or ng of PCDDs per m^3 of stack gas sampled are attainable.

Generation, Emission and Control of Dioxins from Combustions Processes

- PCDDs are probably present in effluents from most, if not all, municipal and industrial waste incinerators. Data are insufficient to establish whether they are generally present in fossil-fuel fired combustion source effluents.

- The available data are insufficient to confirm or refute hypotheses concerning precursors of PCDDs in the incinerator influents. Polychlorophenols and polychlorobenzenes are considered potential precursors for the PCDD emission because PCDDs have been formed from these compounds in laboratory studies.

- Most reports are for analysis of a single sample per facility, usually a sample of fly ash collected by an electrostatic precipitator from hot flue gas. Results may not be representative of potential PCDD emissions from the stack.

- Potential approaches to control of PCDD emissions have been identified; feasibility cannot be evaluated in the absence of criteria that define the degree of control required.

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THE KINETIC ANALYSIS OF TDAS/TDU DATA AND ITS APPLICATION TO PERMITTING OF INCINERATORS

F. C. WHITMORE
Versar Inc.
Springfield, VA

R. A. CARNES
U. S. Environmental Protection Agency
Cincinnati, OH

ABSTRACT

The Thermal Destruction Unit (TDU) and a later version, the Thermal Decomposition Analytical System (TDAS), have been used by researchers at the University of Dayton Research Institute to determine the time-temperature conditions that are required for the thermal degradation of various refractory chemicals. This paper will attempt to show that these data can be used to predict the time-temperature regimen that is required for any preassigned destruction efficiency (DE) without the need for extensive data taking. Further, several other areas of application of the TDU will be discussed.

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INTRODUCTION

The fact that an incineration test burn is an expensive method for the determination of the most appropriate conditions for the satisfactory incineration of a given waste has led to the search for alternate methods by which these conditions can be estimated. Probably the most promising of these alternatives is the Thermal Decomposition Analytical System (TDAS) developed by the University of Dayton group (1). The details of this system have been fully described elsewhere (2) so that a full discussion is not necessary here. Suffice it to say that the system consists of a volatilization chamber, the reactor and its controller, a cryogenic trapping system and the analytical system. The volatilization chamber serves to volatilize the test chemical and insure that the vapor is well mixed with the combustion atmosphere (the composition of the latter can be widely varied). The well mixed gases are then conducted into the reaction chamber wherein they are exposed to precisely known temperatures for a predetermined time. The residual gases are then conducted to the cryogenic trap where the higher molecular weight components are trapped for later analysis. On desorption, the eluted components are passed through a GC and eventually into a MS for identification and quantification.

In a recent report from the Dayton Group (3), careful measurements of the effective destruction efficiency (DE) are presented for the isomer 2,2',4,5,5' -pentachlorobiphenyl for various temperatures and residence times, as shown on Table 1. If it is assumed that the reaction which results in the

Table 1(3)

Fraction Remaining for 2,2',4,5,5'-Pentachlorobiphenyl Versus Temperature for Various Atmospheres

Atmosphere	Fraction Remaining at Specified Temperatures*											
	923°K	948°K	973°K	998°K	1023°K	1048°K	1073°K	1098°K	1123°K	1148°K	1173°K	1198°K
40% O_2 in N_2	.85	.65	.27	.011	.0005							
21% O_2 in N_2	.98	.80	.53	.093	.0005	.00007						
2.5% O_2 in N_2	.97		.91		.83	.37	.12	.004				
100% N_2				1.00		.89		.66		.54	.40	.18
100% He*										.76		.44

*Residence time 2 sec. except helium test, in which residence time was 1.2 sec.

disappearance of the target molecule is pseudo-first order, it becomes possible to estimate the rate constant and its temperature dependence. In this context, it should be noted that the TDAS is normally used to determine the residual concentration of the target molecule and the final combustion products are usually not determined. As a direct extension of these data, it is possible to derive the detailed time-temperature relationship for this particular PCB isomer. The discussion below is devoted to that derivation.

The TDAS and its simpler configuration, the Thermal Destruction Unit (TDU), are similar in operation except for the analytical techniques used. It is the purpose of this paper to show that the TDU can be used to estimate the activation energy and therefore the time-temperature requirements of a given chemical for a preassigned DE. At least two runs of temperature versus DE for fixed residence time under different atmospheric compositions are needed for the analysis. Based on the results obtained, it appears that the TDU represents a very promising technique for preliminary determination of proper operating conditions for safe incineration of a given waste.

The convention by which the TDU data are presented (3) is such as to obscure the asymptotic approach to the temperature axis for values of DE near unity. It can be seen from Figure 1, which is a plot of the time-temperature relationship at preassigned values of DE for the 2,2'4,5,5' -pentachlorobiphenyl isomer, that small changes in temperature, at fixed residence time, can have a large effect on the resulting DE.

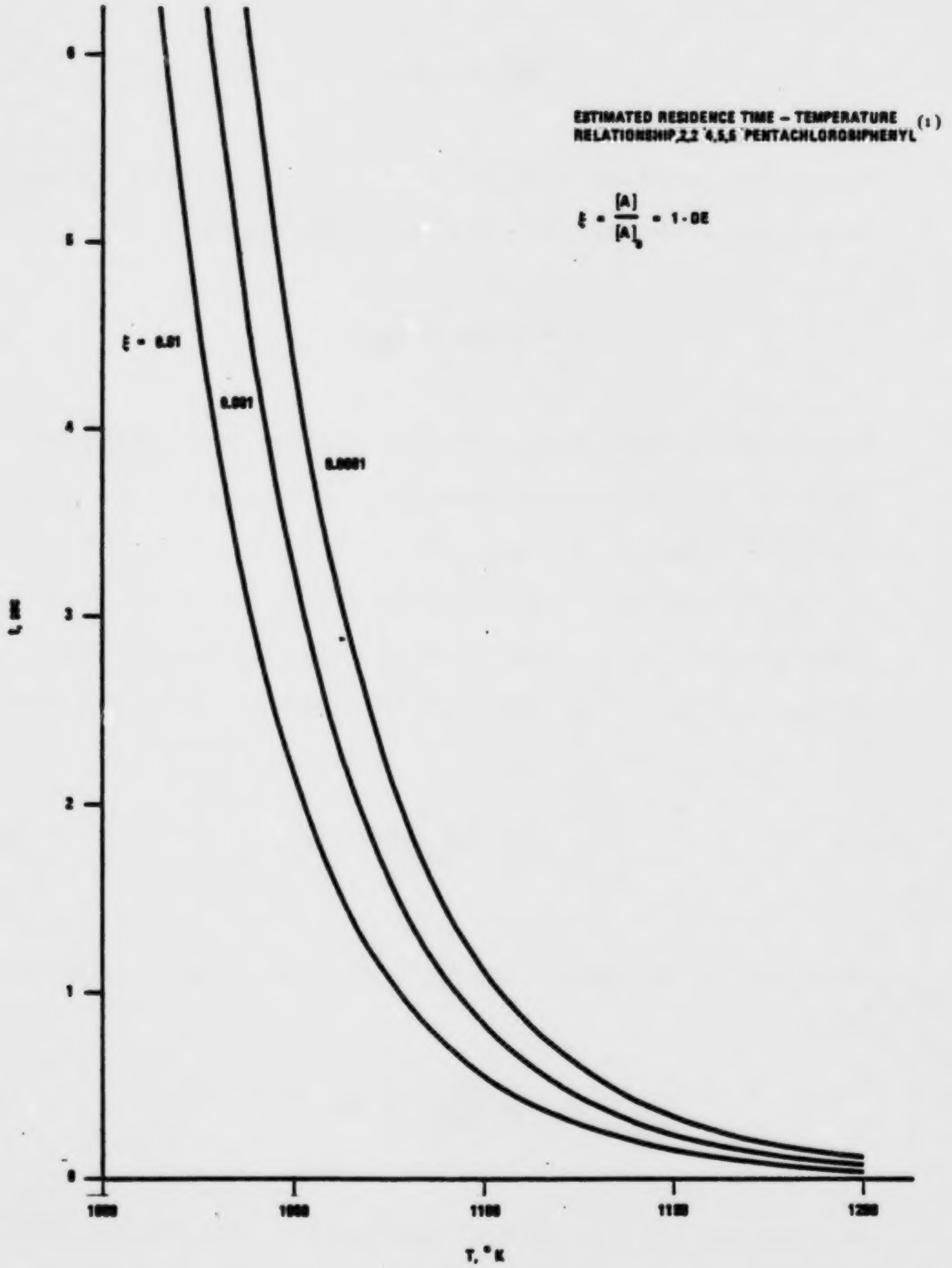
ESTIMATED RESIDENCE TIME – TEMPERATURE RELATIONSHIP,2,2′4,5,5′ PENTACHLOROBIPHENYL (1)
$\xi = \frac{[A]}{[A]_0} = 1 - DE$
ξ = 0.01
0.001
0.0001
t, sec
0
1
2
3
4
5
6
1000
1050
1100
1150
1200
T, °K

FIGURE 1.

The kinetics of a first order reaction may be expressed by the relationship

$$\frac{d[A]}{dt} = -k[A]; \qquad (1)$$

where the reaction rate constant, k, is related to the temperature through the Arrhenius equation,

$$k = Z \exp\left(-\frac{E}{RT}\right). \qquad (2)$$

The parameters in Equations (1) and (2) are identified as follows: E = activation energy, R = universal gas constant; T = absolute temperature, and the prefactor Z is the Arrhenius frequency factor. The [A] represents the concentration of the target molecule at time t where $[A]_o$ is the initial concentration. The solution of Equation (1) takes the form

$$[A] = [A]_o \exp(-kt) \qquad (3)$$

from which, on taking the natural logarithm of both sides, we find

$$\ln \frac{[A]}{[A]_o} = -kt \qquad (4)$$

Now the definition of the destruction efficiency, DE, is

$$\mathrm{DE} = \frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}}$$

which, in terms of the $[A]$ and $[A]_o$ becomes

$$\mathrm{DE} = \frac{[A]_o - [A]}{[A]_o} = 1 - \frac{[A]}{[A]_o}$$

hence,

$$\frac{[A]}{[A]_o} = 1 - \mathrm{DE}. \qquad (5)$$

If we now combine Equation (4) and Equation (5) with the natural logarithm of Equation (2) the result is

$$\ln \left\{ - \ln(1 - \mathrm{DE}) \right\} = \ln\ (Zt) - E/RT$$

which can be re-arranged into the form

$$-\ln(t) = \ln(Z) - \ln \left\{ - \ln(1 - \mathrm{DE}) \right\} - E/RT \qquad (6)$$

The data on the PCB isomer, 2,2',4,5,5' -pentachlorobiphenyl (referred to below as PCB) from the Dayton Group (3) allows the conclusion that the following parameters are characteristic of this species in air (21% O_2):

$$Z - 2.26 \times 10^{13}\ \mathrm{sec}^{-1}$$

$$E/R = 31.5 \times 10^{3}\ {}^{\circ}\mathrm{K}.$$

On substitution of these parameters into Equation (6) we may define the time-temperature relationship for this specific PCB isomer. The result is displayed in Equation (7) and plotted, for several different DE values, in Figure 1.

$$-\ln(t) = 30.75 - \ln\left\{-\ln(1 - DE)\right\} - \frac{31.5 \times 10^3}{T} \qquad (7)$$

THE EFFECT OF VARIOUS ATMOSPHERIC COMBINATIONS ON THE OBSERVED DE

The Arrhenius factor, Z, is given by the following expression for a mixture of gases:$^{(4)}$

$$Z_{A,B} = (n_A + n_B)\sigma^2_{AB}\left\{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)\right\}^{1/2} \qquad (8)$$

where n_A and n_B represent the number density of components A and B respectively; σ^2_{AB} is the collision cross-section of the molecules A and B given by $\sigma = r_1 + r_2$ where the hard sphere model is used and M_A and M_B are the molecular weights of A and B, respectively. The number density of the target molecule is n_A and $n_A/n_B \ll 1$, whereupon Equation (8) takes the form

$$Z_{A,B} \sim n_A\sigma^2_{AB}\left\{8\pi RT\left(\frac{M_A + M_B}{M_A M_B}\right)\right\}^{1/2} \qquad (8')$$

As has been pointed out above, the TDU measurements focus on the disappearance of the target molecules and not on the specific processes by which they disappear. When we consider the effect of a mixture of gases we will assert that there are (at least) two different processes by which the target molecule may be removed. In those collisions which a molecule which itself cannot react with the target molecule (N_2, He) we assume that the disappearance of the target molecule results from the transfer of energy during the collision into internal modes of the target molecule and the subsequent breakup (or alteration) of the target molecule. For those collisions with a molecule which is capable of direct reaction with the target (O_2) , the alteration of the target molecule is assumed to result from a combination of the formation of a compound molecule with internal energy. It is further assumed that the activation energy for these different processes might be quite different. As will be seen, these assumptions are, at least partially, validated by the agreement between experimental data and calculated results.

In a mixed gas environment, that is a mixture of O_2 and N_2 we assume that the measured effect on the target molecule depends on whether the first effective collision is with an oxygen molecule or with a nitrogen molecule. The Arrhenius factors are:

$$Z_{A,O_2} = n_{O_2} \sigma^2_{A,O_2} \left\{ 8\pi RT \left(\frac{M_A + 32}{32 M_A} \right) \right\}^{1/2}$$

$$Z_{A,N_2} = n_{N_2} \sigma^2_{A,N_2} \left\{ 8\pi RT \left(\frac{M_A + 28}{28 M_A} \right) \right\}$$

Now $\sigma^2_{A,B}$ depends on the effective diameters of A and B (4) and, since M_A is greater than M_B (A here refers to the PCB), it is assumed that $\sigma^2_{A,O_2} \sim \sigma^2_{A,N_2}$.

The ratio $Z_{A,O_2}/Z_{A,N_2}$ is then given as

$$\frac{Z_{A,O_2}}{Z_{A,N_2}} \sim \frac{n_{O_2}}{n_{N_2}} \left\{\frac{28}{32}\left(\frac{326.5 + 32}{326.5 + 28}\right)\right\}^{1/2}$$

which, on substitution of MA = 326.5, becomes

$$\frac{Z_{A,O_2}}{Z_{A,N_2}} = 0.941 \frac{n_{O_2}}{n_{N_2}} \tag{9}$$

We may now write the equation describing the combined effects of a mixture of gases as follows:

$$- \ln\frac{[A]}{[A]_o} = k_{eff}t = tZ_{eff} \exp\left(- \frac{E_{eff}}{RT}\right) \tag{10a}$$

and

$$- \ln\frac{[A]}{[A]_o} = k_{O_2}t + k_{N_2}t = tZ_{A,O_2} \exp\left(- \frac{E_{O_2}}{RT}\right) + tZ_{A,N_2}\exp\left(- \frac{E_{N_2}}{RT}\right) \tag{10b}$$

The essential difference between Equation (10a) and (10b) lies in the fact that Equation (10a) describes the experimental facts as observed by the TDU whereas Equation (10b) is a result of the assumption of there being two different types of processes that can lead to the observed experimental facts. The data earlier indicated may now be redefined as, for the mixture of 21% O_2 in N_2:

$$Z_{eff} = 2.26 \times 10^{13} \text{ sec}^{-1}$$

$$\frac{E_{eff}}{R} = 31.5 \times 10^{3} \text{ °K.} \tag{11}$$

Equation (10b) may now be particularized for the PCB to be

$$-\ln\frac{[A]}{[A]_o} = tZ_{A,N_2}\left\{0.941\frac{n_{O_2}}{n_{N_2}}\exp\left(-\frac{E_{O_2}}{RT}\right)+\exp\left(-\frac{E_{N_2}}{RT}\right)\right\} \qquad (12)$$

From the data in Table 1, for the situation with $n_{O_2} = 0$, we may compute from Equation (12),

$$Z_{A,N_2} = 3.3 \times 10^{13}\ \mathrm{sec}^{-1}$$

$$E_{A,N_2}/R = 33.4 \times 10^{3}\ {}^\circ\mathrm{K}. \qquad (13)$$

If we now combine the data in Equation (11) which has taken for 21% O_2 in N_2 with that in Equation (13) for pure nitrogen with Equation (10b) we may compute the activation energy for O_2 to be

$$E_{O_2}/R = 30.0 \times 10^{3}\ {}^\circ\mathrm{K} \qquad (14)$$

We may combine these results to yield the general expression

$$-\ln\left\{\frac{[A]}{[A]_o}\right\} = 6.6\mathrm{x}10^{13}\left\{0.941\frac{n_{O_2}}{n_{N_2}}\exp\left(-\frac{30\mathrm{x}10^{3}}{T}\right)+\exp\left(-\frac{33.4\mathrm{x}10^{3}}{T}\right)\right\} \qquad (15)$$

which should be applicable for this specific PCB isomer for any combination of atmospheres. To illustrate the validity of the above analysis, the theoretical values of $[A]/[A]_o$ (as derived from Equation (15) are plotted against the experimental values from the Dayton Group (3) (where t = 2 sec.). The results are shown in the Figures 2,3, and 4, and show that the agreement is very good.

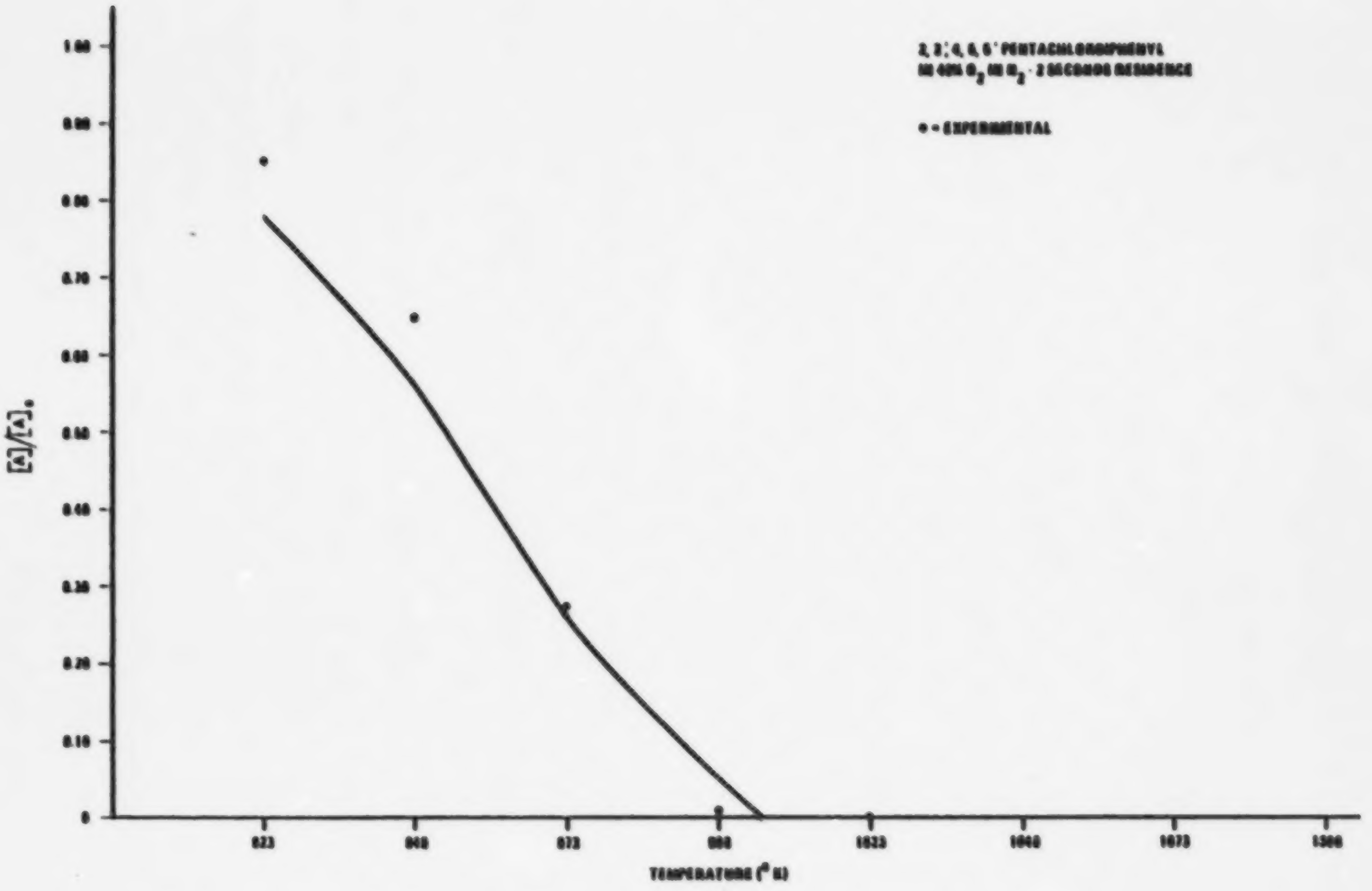
2, 2', 4, 5, 5' PENTACHLOROBIPHENYL
IN 40% O_2 IN N_2 · 2 SECONDS RESIDENCE
● - EXPERIMENTAL
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
$[A]/[A]_o$
923
948
973
998
1023
1048
1073
1098
TEMPERATURE (° K)

FIGURE 2.

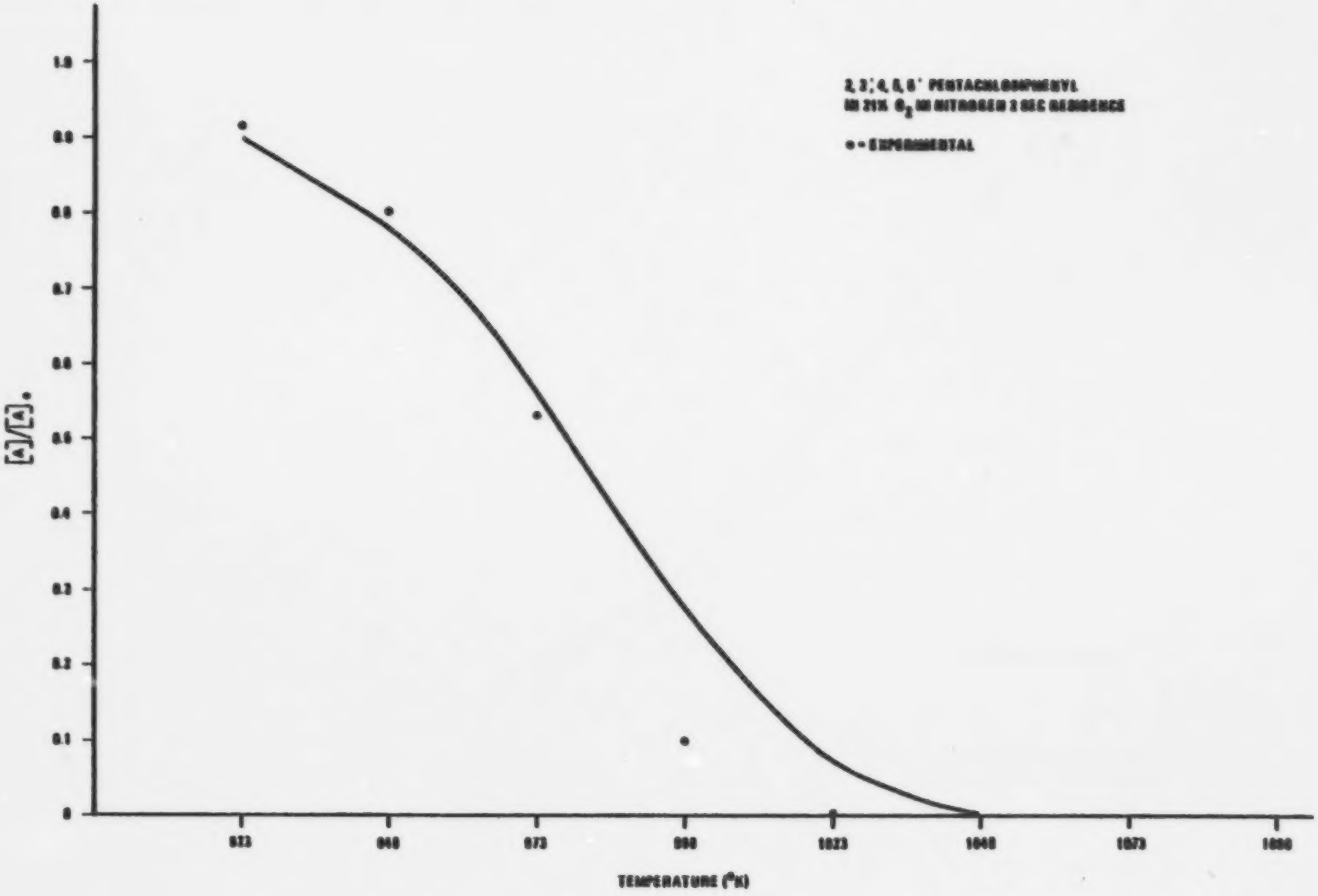
2,3',4,5,6' PENTACHLOROBIPHENYL
IN 21% O_2 IN NITROGEN 2 SEC RESIDENCE
● = EXPERIMENTAL
[A]/[A]o
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
923
948
973
998
1023
1048
1073
1098
TEMPERATURE (°K)

FIGURE 3

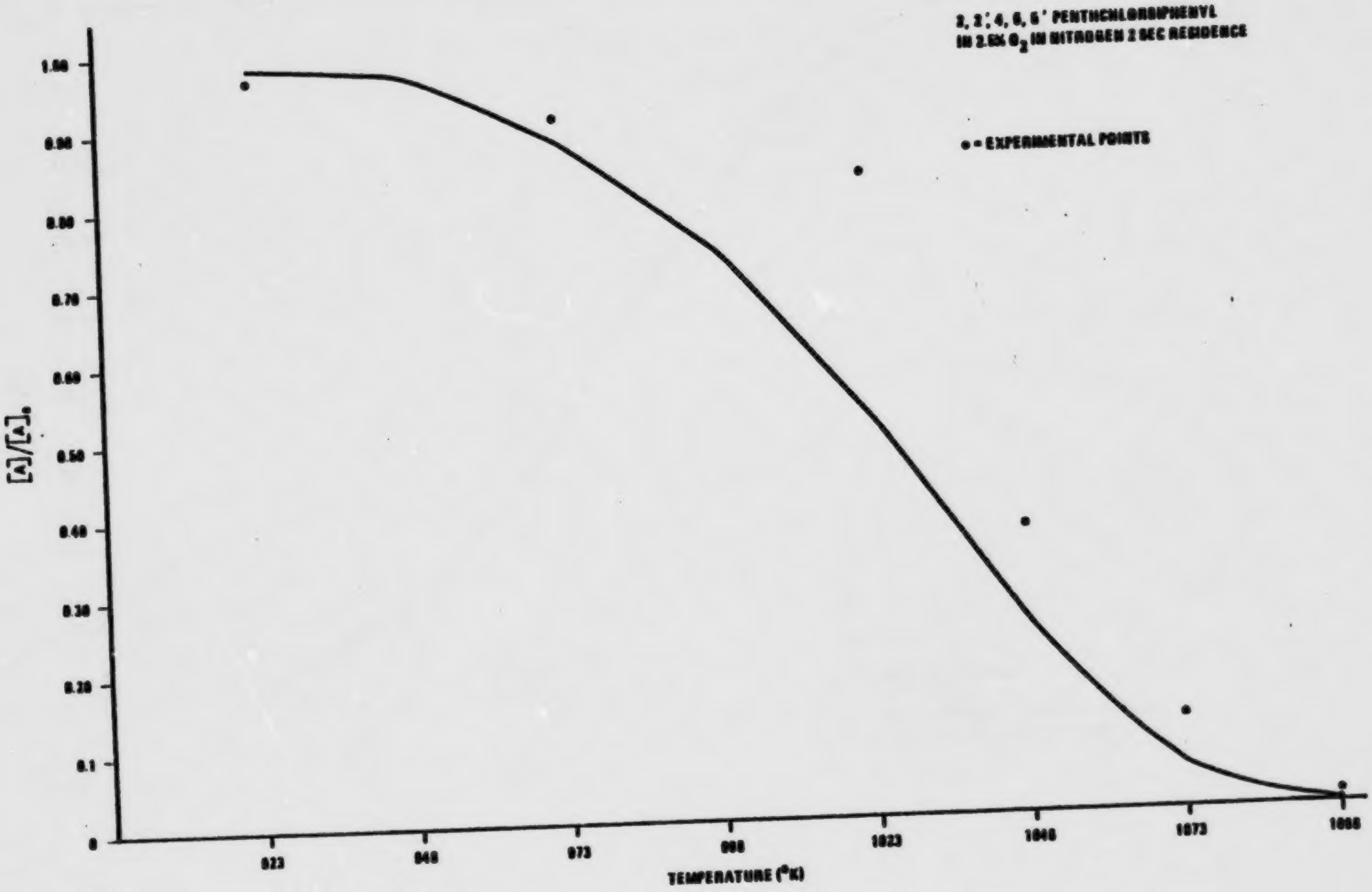
2, 2', 4, 6, 6' PENTACHLOROBIPHENYL
IN 2.5% O_2 IN NITROGEN 2 SEC RESIDENCE
● = EXPERIMENTAL POINTS
$[A]/[A]_o$
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.1
0
923
948
973
998
1023
1048
1073
1098
TEMPERATURE (°K)

FIGURE 4.

A POSSIBLE EXPLANATION OF THE OBSERVED LARGE SCALE EFFECTS

It has been noted many times that one difficulty with the TDU data lies in the fact that the actual temperatures that are needed in a large scale system seem to be significantly higher than those indicatedby the TDU experiments. To illustrate one possible explanation for this observation, we consider the effect of incinerating 2,2',4,5,5' -pentachlorobiphenyl in a mixture of 3% O_2, 12% CO_2 and 85% N_2. Here again, we assume that the effective activation temperature (E/R) for CO_2 collisions is the same as that for N_2 collisions, and weight the relative concentrations as before. We again apply Equation (10b) modified to include the effects of CO_2 to find

$$-.\ln\left\{\frac{[A]}{[A]_o}\right\} = 6.6\text{x}10^{13}\left\{1.14\exp\left(-\frac{33.4\text{x}10^3}{T}\right) + 0.035\exp\left(-\frac{30\text{x}10^3}{T}\right)\right\}$$

The results of a series of calculations using Equation (16) are tabulated in Table 2.

Table 2

Values of $\ln\frac{[A]}{[A]_o}$ for Pentachlorophenyl in 12% CO_2, 3% O_2 and 85% N_2

T (°K)	$\ln[A]/[A]_o$	DE
923	- 0.0305	0.03
948	- 0.083	0.08
973	- 0.186	0.17
998	- 0.431	0.35
1023	- 0.916	0.60
1048	- 1.966	0.86
1073	- 3.91	0.98
1098	- 7.78	0.99958
1123	- 14.9	0.9999997

From the computed DE values in Table 2, it is clear that small variations in exposure temperature can have very significant effects on the attainable DE.

CONCLUSIONS

The goodness of fit between the theoretical estimates of DE and the experimental data suggests that this simplified model has features that approximate the real situation. The marked dependence of DE on temperature, especially at the upper temperatures at which DE approaches values acceptable for field scale systems, indicates one possible explanation for the observed differences between laboratory data and field scale data. It should also be noted that the DE at a given temperature is highly dependent on the composition of the combustion atmosphere. When one considers the statistical variations to be expected in both temperature and localized atmosphere composition, it is not surprising that there are significant variations observed in the DE from practical scale systems.

In the future we will attempt to extend this analysis to a more detailed discussion of the conditions that are expected to exist in a full scale incinerator and the effects that such conditions will have on the successful combustion of refractory compounds.

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COMBUSTION RATE PREDICTIONS FOR CONTROLLED-AIR INCINERATOR

D. I. ORLOFF
University of South Carolina
Columbia, SC

H. E. HOOTMAN
E. I. duPont de Nemours & Company
Aiken, SC

ABSTRACT

The Savannah River Laboratory (SRL) is developing incineration processes to reduce the storage volume of combustible solid process waste. A ceramic, two-stage, controlled-air incinerator that is electrically heated has been developed for volume reduction of waste contaminated with high-level alpha emitters. In addition, a controlled-air incinerator is being developed to handle large quantities of waste contaminated with low level beta-gamma emitters. This paper presents a computational method to predict combustion air and combustion chamber volume requirements as a function of waste feed composition, waste package size, and throughput. The method is based on a combustion rate model which requires waste thermophysical data that are generally available in the literature.

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INTRODUCTION

Prediction of the limiting values of incineration, such as combustion air requirement and waste heat release, is more important in radioactive waste applications than in conventional waste incineration. A radioactive waste incinerator should not be allowed to become air starved because the resulting soot will foul the exhaust HEPA filters and interrupt off-gas flow. Excessive heat release will damage the incinerator and off-gas equipment or severely limit waste throughput during sustained operation. These conditions result in additional radiation exposure to operating personnel and significantly increase radioactive secondary waste generation from the incineration process.

Pyrolysis and combustion rates were measured on a laboratory-scale incinerator for latex, cellulose, and polyethylene as a function of incinerator wall temperature and inlet gas flow rate. It was shown that wall temperature had a strong effect on pyrolysis and combustion rates, but that inlet airflow had no effect on combustion rates. The data from this study were used to develop an incinerator burning rate model [1]. The model proved successful in predicting the observed burning rates in the laboratory-scale incinerator for single component polymer wastes. This paper describes the application of the model to the 0.5 kg/hr pilot and 5 kg/hr full-scale prototype incinerators and compares the computed results with test data. For all variables used in the equations, refer to the nomenclature for definitions.

ANALYTICAL MODEL

The objective of the modeling effort was to predict the transient waste burning rate and air requirement for the controlled-air incinerators (as a function of waste composition) and incinerator operating conditions. The model was developed for a plane dimensional geometry and then modified for the case of a cylinder with a decreasing diameter.

Two interdependent models are developed in this section: a phenomenological pyrolysis model and a mass burning rate model. Figure 1 identifies the pertinent variables for the one-dimensional problem. In a heated enclosure with transverse nitrogen flow, a flat polymer surface will absorb heat by thermal radiation and convection as

$$Q = \sigma F_{ws} \frac{A_w}{A_s} (T_w^4 - T_s^4) + h\,(T_\delta - T_s) \qquad (1)$$

In the incinerators of interest in this study, the last term (convection term) may be neglected. If the net heat flux to the polymer surface is assumed to be uniform and the polymer surface at a temperature, T_s, then

$$Q = r\rho \left[C_{pp} (T_s - T_\infty) + L_s \right] = r\rho L_g \qquad (2)$$

where r is the regression rate, and L_g is the effective heat of gasification of the polymer. Employing continuity at the polymer surface, the pyrolysis rate is given by

$$\dot{m}_p = rA_s\rho \qquad (3)$$

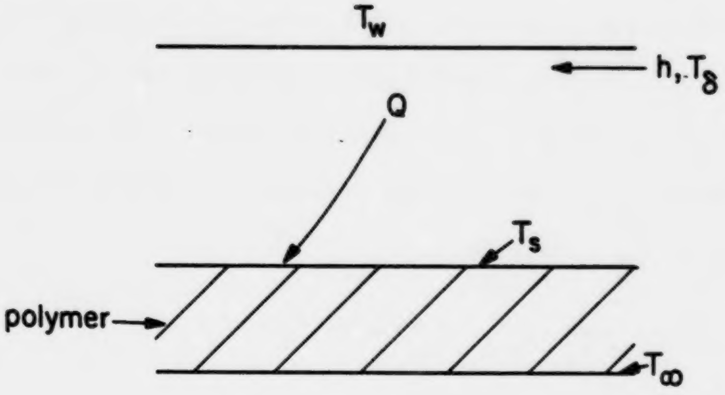
T_w
h, T_δ
Q
T_s
polymer
T_∞

Figure 1. Schematic of Pyrolysis Process

Combining equations (1), (2) and (3) yields

$$\dot{m}'' = \frac{\dot{m}_p}{A_s} = \frac{\sigma F_{ws} \frac{A_w}{A_s} (T_w^4 - T_s^4)}{L_g} \tag{4}$$

Implied in this phenomenological approach is the approximation that the characteristic polymer surface temperature, T_s, is independent of the heat flux to the polymer surface. Since T_s only affects the back radiation term, which is small for our application, this approximation is justified. In addition to the effective heats of gasification and characteristic surface temperature measured in earlier work [1], values for other polymers have been reported in the literature [2].

As an approximation, which has been tested experimentally, the effective heats of gasification and characteristic surface temperatures of polymer mixtures were estimated assuming no interaction between polymers during pyrolysis as

$$L_{g_{mix}} = \Sigma M_j L_{gj} \tag{5}$$

$$T_{s_{mix}} = \Sigma M_j T_{sj} \tag{6}$$

In the presence of overfire air in a heated enclosure, a flat polymer surface will pyrolyze as described previously. However, in addition to net thermal radiation from the enclosure to the polymer surface, heat will also be transferred from the flame above the polymer to the polymer surface by flame radiation and conduction. In addition, the flame may partly block thermal radiation from the enclosure to the polymer. For the dimensions of the incinerators considered in this paper, the mean path length is small; therefore, flame radiation may be neglected in the analysis. For the case of an externally applied heat flux to a polymer with transverse airflow, the polymer mass burning flux may be determined from diffusion flame theory [3-6] as

$$\dot{m}'' = \frac{K}{\delta C_p} \ln \left(1 + \frac{B}{1-E}\right) \tag{7}$$

where the external heat transfer parameter, E, is given by

$$E = \frac{Q}{\dot{m}'' L_g} \tag{8}$$

and the mass transfer number, B, may be defined as

$$B = \frac{i \left(M_{O_2}\right)_\infty \Delta H_c + C_p \left(T_w - T_s\right)}{L_g} \tag{9}$$

where the mass stoichiometric index, i, is defined by the single-step stoichiometric relation i grams of polymer + 1 gram of oxygen yields (1 + i) grams of product ($CO_2 + H_2O$), and ΔH_c is the heat combustion of the polymer. Combining equations (7), (8) and (9) yields

$$\dot{m}'' = \frac{1}{\delta}\left(\frac{K}{C_p}\right) \ln \left\{ \frac{1 + i \left(M_{O_2}\right)_\infty \Delta H_c + C_p \left(T_w - T_s\right)}{L_g - \left(\frac{\sigma F_{ws} \left(A_w/A_s\right)\left(T_w^4 - T_s^4\right)}{\dot{m}''}\right)} \right\} \tag{10}$$

Equation (10) may be used to predict the polymer mass burning flux once the diffusion layer thickness, δ , is evaluated. In the incinerators of interest in this paper, free convection dominates

dominates forced convection, and the diffusion layer thickness is independent of transverse airflow rate. Employing standard heat transfer correlations for the case of laminar free convection [7],

$$\frac{1}{\delta} = 0.91\left(\frac{PM}{\bar{R}\mu_f}\right)^{1/2}\left[\frac{g\,(T_{f1} + T_s)}{T_{f1}\,(T_{f1} + T_s)^2\,2d}\right] \tag{11}$$

equation (11) may be substituted into equation (10) and $\dot{m}''$ solved by the Newton-Rhaphson method. This solution will hold at low and moderate incinerator wall temperatures, T_w. At high wall temperatures the problem becomes fully radiation-controlled, and the radiation heat transfer parameter, E, becomes unity. Hence, at very high wall temperatures, the polymer mass burning flux may be predicted by equation (4).

The equations have been developed for a flat polymer surface burning in an incinerator with transverse overfire air at low to moderate velocities. The model required knowledge of the flame temperature at theoretical air conditions, T_{f1}, the effective heat of gasification of polymer, L_g, and the characteristic polymer surface temperature, T_s.

EXTENSION OF THE MODEL TO TIME-DEPENDENT CYLINDRICAL GEOMETRY

Each pilot and full-scale incinerator has a cylindrical refractory primary chamber surrounded by electrical girdle heaters. Cylindrical paper-wrapped waste packages were inserted into the primary chamber as shown in Fig. 2. In transforming the planar model to cylindrical geometry, it has been assumed that the

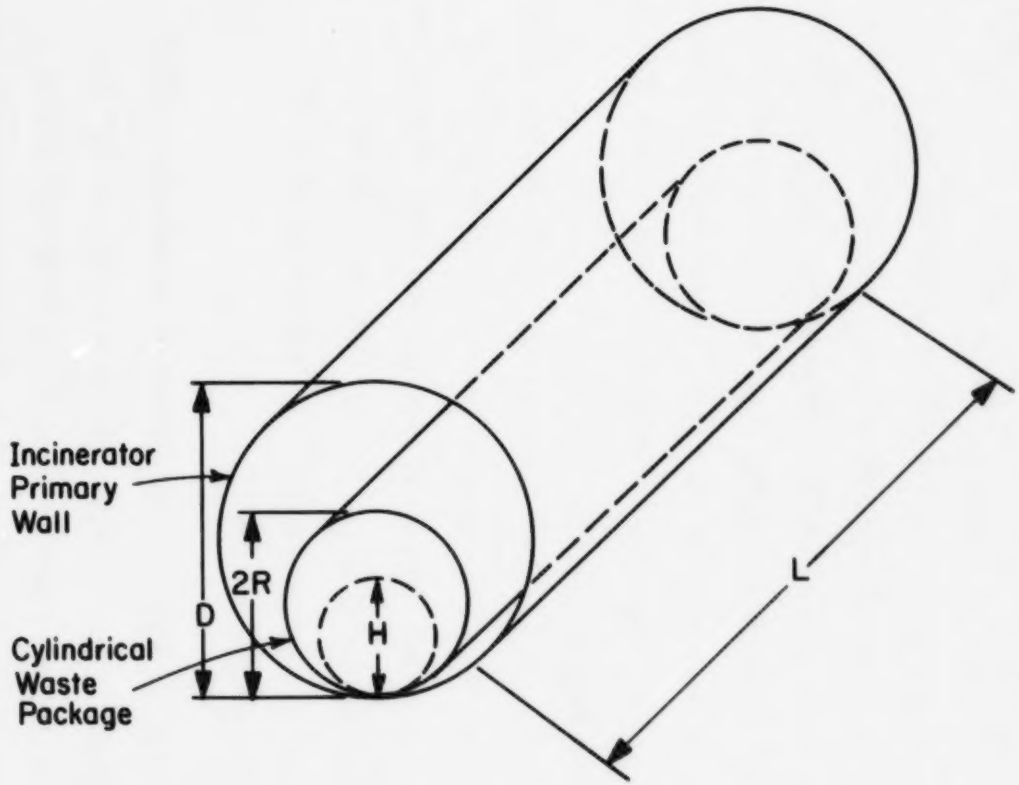
Incinerator
Primary
Wall
Cylindrical
Waste
Package
D
2R
H
L

Figure 2. Geometry of the Primary Chamber and Waste Package

change in package length is small relative to the change in diameter. Conversion to cylindrical geometry involves the following substitutions in the one-dimensional model

$$A_w = \pi DL \tag{12}$$

$$A_s = \pi HL \tag{13}$$

where H is the regressed diameter. In addition, the characteristic waste dimension, d, may be defined as

$$d = \frac{L + H}{2} \tag{14}$$

Assuming that the waste polymers are black, the angle factor between the enclosure and polymer surface may be determined as

$$F_{ws} = \left[\frac{1}{\epsilon_w} - 1 + \frac{A_w}{A_s}\right]^{-1} \tag{15}$$

For a given incinerator primary of diameter, D, and wall temperature, T_w, and for a particular waste polymer or polymer mixture, the polymer mass burning flux, $\dot{m}''$, may be calculated for various regressed diameters, H. This relationship may then be fit by the method of least squares to the form

$$\dot{m}'' = K_o H^{K_1} \tag{16}$$

where K_o and K_1 are correlation coefficients. The instantaneous polymer burning rate can then be expressed as

$$\dot{m}_f = \dot{m}'' A_s \tag{17}$$

Employing equations (13), (16), and (17) yields

$$\dot{m}_f = K_o \pi L H^{K_1 + 1} \tag{18}$$

The instantaneous polymer mass is

$$m_f = \rho \frac{\pi}{4} H^2 L \tag{19}$$

Differentiating equation (19) and recognizing that

$$\dot{m}_f = - \frac{dm_f}{dt} \qquad (20)$$

yields

$$\dot{m}_f = - \rho \frac{\pi}{2} LH \frac{dH}{dt} \qquad (21)$$

Combining equations (18) and (21) and integrating with the following initial condition

$$t = 0 \qquad H = 2R \qquad (22)$$

yields

$$H = \left[(2R)^{1-K_1} - \left(\frac{2 K_o (1 - K_1)}{\rho} \right) t \right]^{\frac{1}{1-K_1}} \qquad (23)$$

Substituting equation (23) into equation (18) yields an expression for the instantaneous polymer burning rate as a function of time.

$$\dot{m}_f = K_o \pi L \left[(2R)^{1-K_1} - \left(\frac{2 K_o (1 - K_1)}{\rho} \right) t \right]^{\frac{1+K_1}{1-K_1}} \qquad (24)$$

Employing the equations stated above, the burning rate may be calculated as a function of time. The burning rate is used to calculate the energy release from combustion of the waste material or its volatiles and the stoichiometric air required to completely burn the waste materials. These values are proportional to directly input values of heat of combustion, molecular weight of the feed, and the mole ratio of O_2 to feed material.

If pyrolysis rates and not combustion rates are desired, the mass regression rate is given by using equation (4) instead of (10) for $\dot{m}''$.

EXPERIMENTAL MEASUREMENTS

The pilot [8] and full-scale [9] incinerators are electrically heated, controlled-air units with primary and secondary combustion chambers. The waste feed is shredded and packaged in cylindrical paper bags. Typical waste package sizes were one-inch OD by 4 inches long for 20-gram packages in the pilot, and 4-inch OD by 7 inches long for 200-gram packages in the full-scale incinerator. The waste packages were fed through a double-valve air lock and rammed into the center of the silicon carbide horizontal primary chambers. The dimensions of the pilot primary chamber are 4.5-inches ID by 4 feet long. The full-scale primary chamber is 8.5-inches ID by 6 feet long.

The waste package is burned in substoichiometric air at a constant controlled wall temperature from 500 to 900°C. The gases and soot from the primary chamber are drawn by an induced air blower into the secondary combustion chamber where they are completely burned in excess air at a chamber temperature between 800 and 1000°C. The pilot and the full-scale incinerators are equipped with oxygen analyzers at the exit of the secondary combustion chamber. Both incinerators have quartz windows so that the wall temperature can be measured by an optical pyrometer and so that flame duration can be visually determined.

Tests burning 20- and 200-gram packages of latex, PE, PVC, cellulose, and a waste mixture were made on the pilot and full-scale incinerators, respectively. For each run, a graph of oxygen depletion vs. time was recorded from the incinerator exhaust. The flame duration was timed by a stopwatch. This information was used to determine the experimental combustion rate of each material, as shown on Table 1.

Figure 3 compares the oxygen content of exhaust gas as a function of time for single packages of different types of waste and for a typical radioactive waste mixture. Latex rubber shows the greatest oxygen depletion (i.e., requires the most air) and polyvinyl chloride shows the least oxygen depletion (i.e., requires the least air).

Tests were run on the full-scale incinerator using 200-gram packages of 2 to 1 and 1 to 2 mixtures of latex and PE and of latex and PVC. These tests were performed to verify the accuracy of calculated rates with respect to waste component weight percent in the mixture.

Each curve of oxygen depletion was first measured with a planimeter to find its area. This area was then divided by the length of the base to give the average oxygen consumption. The maximum O_2 use was divided by this measured average to obtain a max/avg ratio. This ratio multiplied by the average measured burning rate for the material (g/sec) gives the maximum experimental consumption rate observed for the burning material.

RESULTS

The results of these experiments at a primary wall temperature of 700°C and the prediction of the analytical model are shown in Table 1. Table 2 lists the data that were used in the analysis.

Table 1 Comparison of measured and calculated values

Waste Materials	20 g (Pilot incinerator)		200 g (Full-scale incinerator)	
	Measured	Calculated	Measured	Calculated
Latex rubber				
Maximum rate g/sec	0.45	0.68	1.95	2.06
Average rate, g/sec	0.18	0.15	0.87	0.91
Burn Time, sec	110	103	231	211
Polyethylene				
Maximum rate, g/sec	0.26	0.21	1.03	1.00
Average rate, g/s	0.15	0.12	0.57	0.56
Burn Time, sec	130	160	341	360
Polyvinyl chloride				
Maximum rate, g/sec	0.17	0.13	0.68	0.42
Average rate, g/sec	0.06	0.08	0.25	0.22
Burn Time, sec	350	260	800	900
Cellulose				
Maximum rate, g/sec	0.24	0.14	1.15	0.89
Average rate, g/sec	0.08	0.08	0.46	0.52
Burn Time, sec	250	240	428	380
Waste mixture (a)				
Maximum rate, g/sec	0.19	0.14	1.03	0.68
Average rate, g/sec	0.07	0.07	0.41	0.43
Burn Time, sec	300	290	486	458

(a) 31% cellulose, 27% PVC, 21% PE, 21% latex.

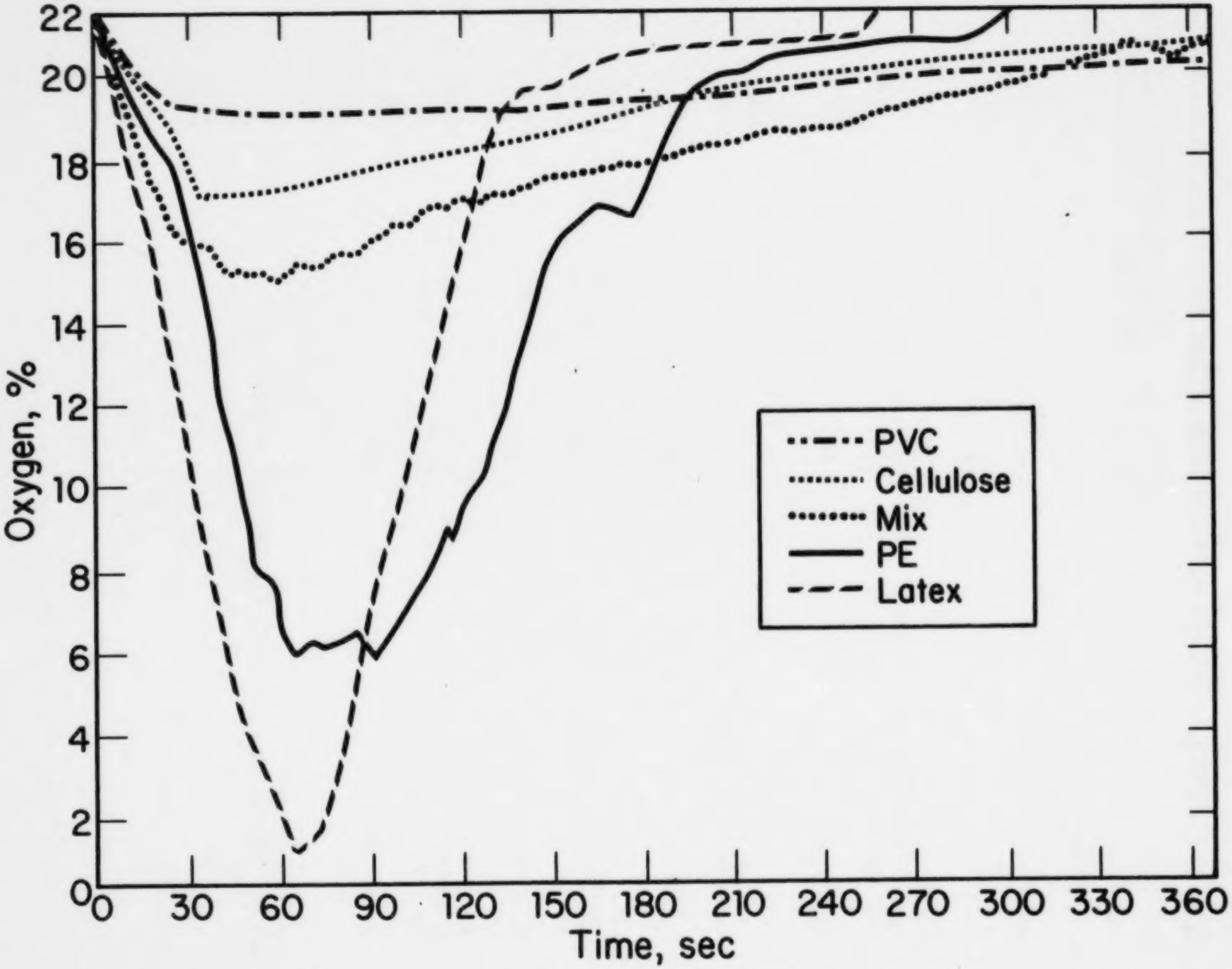

Figure 3. Typical Waste Package Burning Cycle As Determined by Oxygen Depletion in the Full-Scale Incinerator Exhaust

Table 2 Data for full-scale incinerator

Variable	Polyethylene	Latex	Cellulose	PVC
sample wt., g	200	200	200	200
T_w, °C	700	700	700	700
R, cm	4.13	3.81	5.69	5.08
ρ, g/cc	0.21	0.39	0.09	0.23
L, cm	17.8	11.1	21.6	10.8
T_∞, °C	20	20	20	20
ε_w	0.55	0.55	0.55	0.55
L_g, kJ/g	1.13	0.29	2.54	2.50
D, cm	21.6	21.6	21.6	21.6
T_s, °C	475	410	248	507
ΔH_c, J/g	47088	43575	18681	21343
i	0.292	0.3041	0.844	0.781
T_{fl}, °C	1527	1527	1527	1527

The calculated average and maximum polymer burning rates compare favorably with the experimental results from the pilot and full-scale incinerators.

The laboratory-scale incinerator studies showed a strong dependence of burning rate on incinerator wall temperature. In order to test this effect, 100-gram packages of single component waste were incinerated in the full-scale incinerator at various constant incinerator wall temperatures from 500 to 900°C. The experimental results are shown in comparison to the predictions of the model in Figures 4 and 5. The comparison shows agreement.

The assumption was made in the analytical model that each polymer in a mixture of polymers does not interfere with the rate of the other polymers in the mixture. In order to test this hypothesis, experiments were run on the full-scale incinerator using 200-gram packages of various two-component mixtures of latex and polyethylene and of latex and polyvinylchloride. The experiments were performed at an incinerator wall temperature of 700°C as in the previous experiments. Figures 6 and 7 show comparisons of measured and computed maximum and average polymer burning rates for the two mixture types. The model correctly predicts average polymer mixture burning rates but indicates possible interaction in the latex-PVC mixtures.

CONCLUSIONS

The analytical model is in agreement with the measured maximum and average burning rates of major polymer wastes and waste mixtures. The burning transient code has been used to

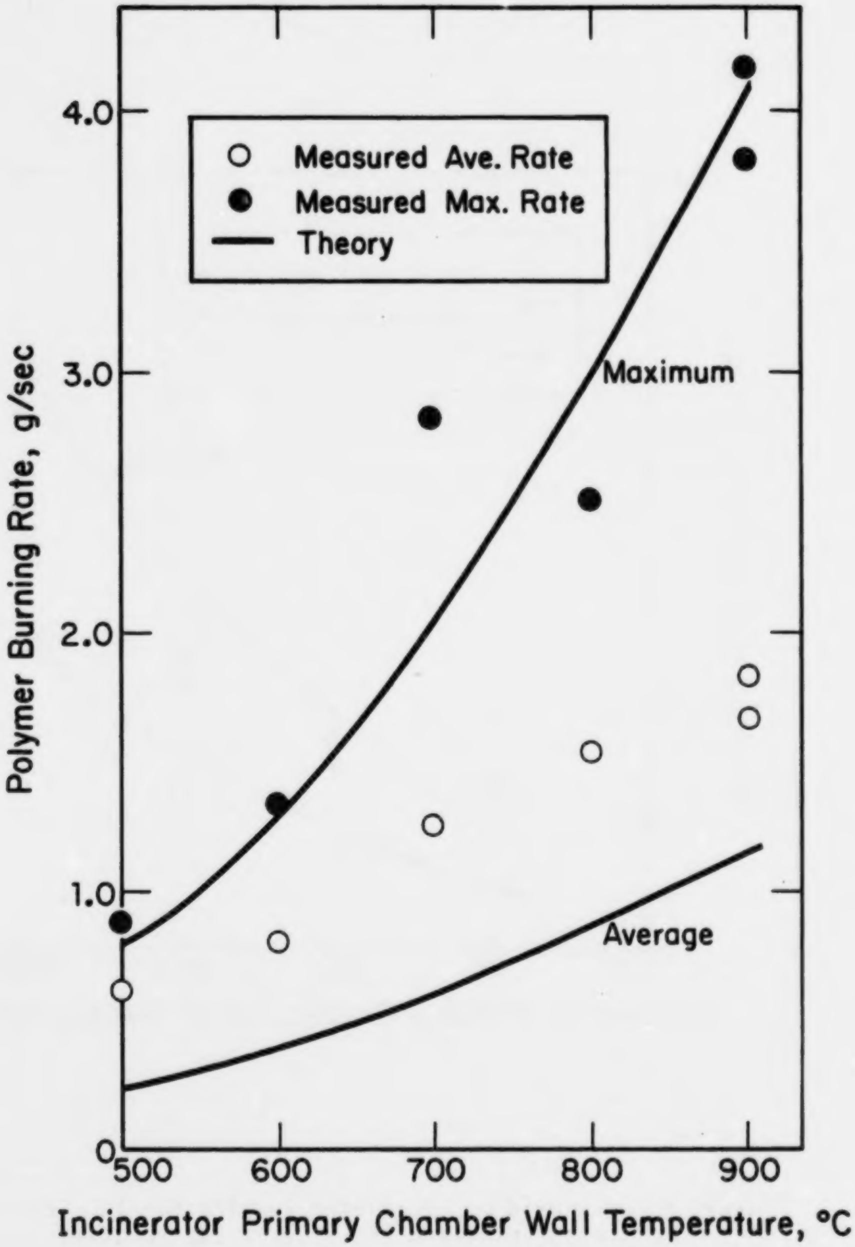

Figure 4. Measured vs Calculated Results for 100-Gram Samples of Latex (Full-Scale Incinerator)

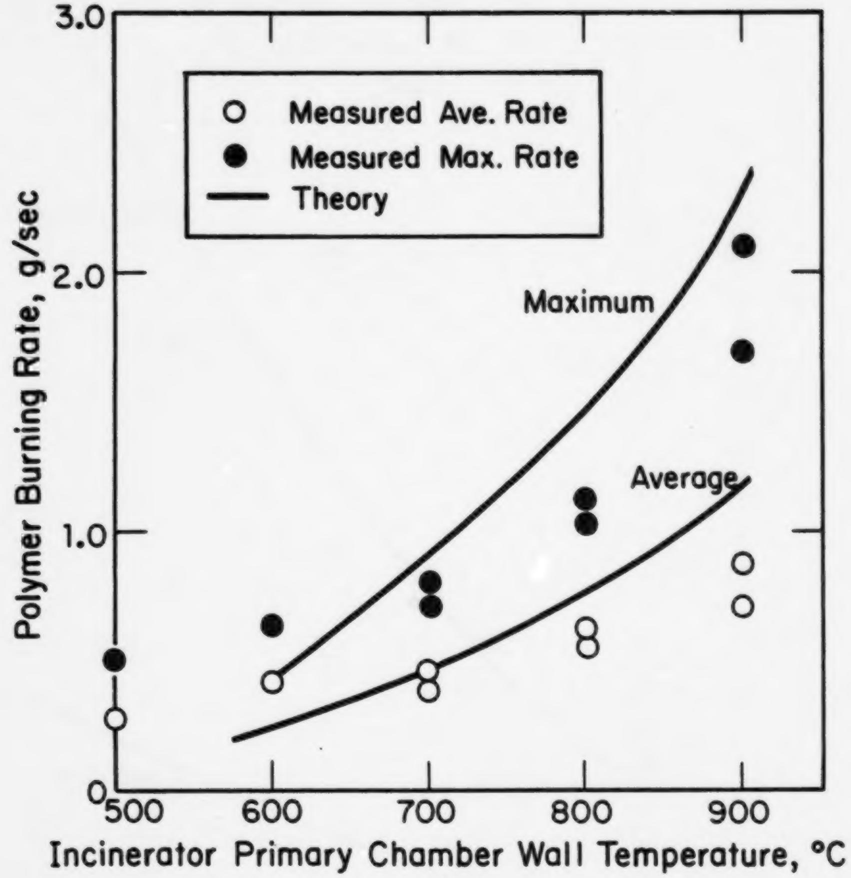

Figure 5. Measured vs Calculated Results for 100-Gram Samples of Polyethylene (Full-Scale Incinerator)

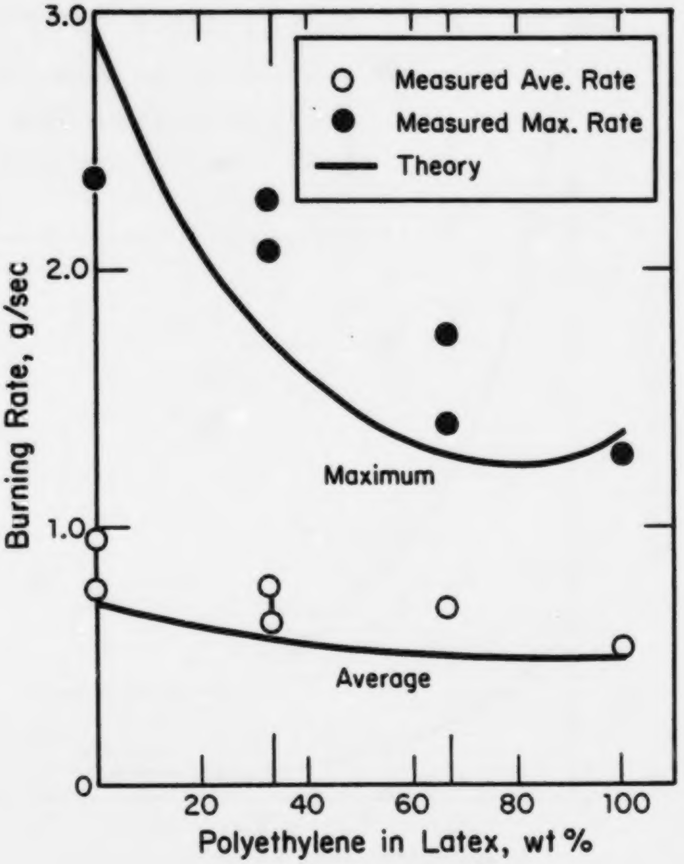

Figure 6. Measured vs Calculated Results for 200-Gram Samples of Polyethylene-Latex Mixtures at 700°C (Full-Scale Incinerator)

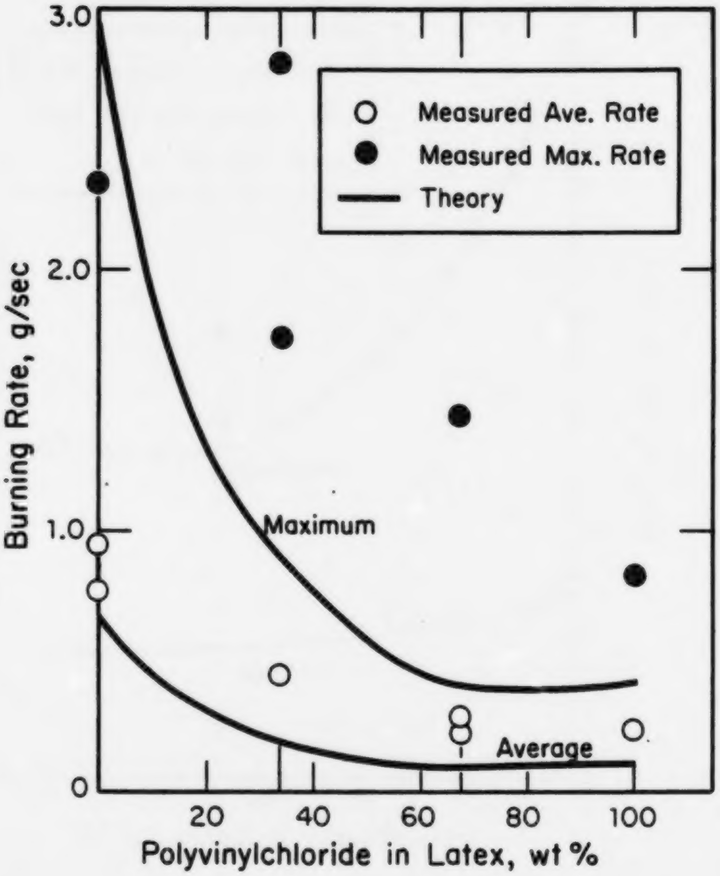

Figure 7. Measured vs Calculated Results for 200-Gram Samples of Latex-Polyvinylchloride Mixtures at 700°C

calculate both the feed-package size limits and the waste-charging frequency limits for excess air combustion in the pilot and full-scale incinerators.

Although the burning rate code gives adequate results with small externally heated waste incinerators, its applicability to large internally heated waste incinerators has not been established. The influence of flame radiation on the present analytical model will be tested this summer in a 180 kg/hr oil-fired, controlled-air waste incinerator.

ACKNOWLEDGEMENT

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NOMENCLATURE

A_s = waste-surface area exposed to the radiant heat flux, m^2

A_w = surface area of primary combustion chamber seen by the waste, m^2

B = Spalding's mass transfer number

C_p = specific heat at constant pressure of gas phase above the waste surface, kJ/g °K

C_{pp} = specific heat of the pyrolyzing waste, kJ/g °K

D = diameter of primary combustion chamber, m

d = waste characteristic length, m

E = external heat transfer parameter

F_{ws} = angle factor between primary walls and the surface of the waste

g = acceleration of gravity, m/sec^2

h = convective heat transfer coefficient

H = regressed diameter of the waste, m

i = mass stoichiometric index

K = thermal conductivity of the gas phase above the waste surface, kJ/m/sec °K

K_o = correlation coefficient

K_1 = correlation coefficient

L = Length of the waste package, m

L_g = "effective" heat of gasification of the polymer waste, kJ/g

L_s = heat of gasification of the polymer waste, kJ/g

M = molecular weight of the inlet gas, g/mol

$(M_{O_2})_\infty$ = mass fraction of O_2 in the primary inlet

M_j = mass fraction of waste j in a waste mixture

$\dot{m}''$ = mass flux of waste being consumed, $g/m^2/sec$

$\dot{m}_p$ = rate of mass loss of waste due to pyrolysis, g/sec

m_f = instantaneous waste mass, g

$\dot{m}_f$ = instantaneous waste burning rate, g/sec

P = pressure inside primary combustion chamber, N/m^2

Q = net heat flux to the polymer surface

$\bar{R}$ = universal gas constant

R = initial radius of waste package, m

r = regression rate, m/sec

T_{fl} = flame temperature, °K

T_s = characteristic polymer surface temperature, °K

T_w = primary combustion chamber wall temperature, °K

T_δ = free stream gas temperature in primary, °K

T_∞ = initial temperature of polymer, °K

t = time, sec

ΔH_c = heat of combustion per unit mass of polymer waste, kJ/g

δ = diffusional layer thickness, m

ρ = density of polymer waste package, g/m^3

μ_f = viscosity of gas phase above the waste surface at the film temperature, g/m/sec

σ = Stefan-Boltzman constant

ϵ_w = emissivity of the primary combustion chamber wall surface

HAZARDOUS AND RADIOACTIVE WASTE INCINERATION STUDIES AT LOS ALAMOS

J. S. VAVRUSKA, L. A. STRETZ and L. C. BORDUIN
Los Alamos Scientific Laboratory
Los Alamos, NM

ABSTRACT

A production-scale controlled air incinerator, using commercially available equipment and technology, has been modified for solid radioactive and hazardous waste service. This unit successfully demonstrated the volume reduction of transuranic (TRU) waste with an average TRU content of about 20 nCi/g. The same incinerator including an offgas treatment system is being modified further to evaluate the destruction of hazardous liquid wastes such as polychlorinated biphenyls (PCB's).

1. INTRODUCTION

Solid wastes, both radioactive and hazardous, which are contained in a combustible matrix often lend themselves to incineration as a viable method of treatment. In the case of radioactive wastes, incineration provides a means of volume reduction. For hazardous wastes, incineration not only reduces the total volume, but renders the waste safe by thermal destruction of the hazardous chemical constituents.

Solid radioactive wastes contaminated with transuranic (TRU) isotopes, primarily plutonium, are routinely generated by Defense-related activities at facilities operated under contract to the US Department of Energy (DOE). These materials result from laboratory, processing, and decommissioning activities, and while small compared to municipal waste volumes, they are significant due to the special handling required for safe disposal. Approximately 8600 m^3 of TRU-contaminated solid waste is generated annually by government facilities as a heterogeneous mixture of cellulosics, plastics, rubber, and a variety of noncombustible materials such as metal, glass, and concrete. The combustible portion constitutes about 45% of this volume.

Since 1970, these wastes have been segregated according to their level of TRU content. Low-level wastes, those whose level of activity is $<10^{-8}$ Ci/g of waste, are committed to shallow earth burial in controlled areas.

In 1973, the Los Alamos National Laboratory established a study program for the development, evaluation, and demonstration of production-scale (50 - 100 kg/hr) TRU waste treatment processes. The initial process investigated was to be incineration-based and utilize commercially available technology for volume reduction and chemical stabilization of low-level activity TRU-contaminated combustible materials. Process evaluation resulted in selection and modification of a controlled air incinerator (CAI) system for the TRU solid waste incineration program at Los Alamos.

This system is equipped with sophisticated containment, safety, and offgas cleanup systems which makes it well suited to hazardous waste incineration studies. Initially, the Los Alamos CAI will evaluate incineration of two types of hazardous wastes: solid pentachlorophenol (PCP)-treated wood, and liquid polychlorinated biphenyls (PCBs).

Incineration under improper conditions or open burning of wood which has been treated with PCP can result in the generation of toxic reaction products in the offgas stream. Various organochlorine compounds have been reported as incomplete combustion products from the burning of PCP-treated wood, including chlorinated dibenzo-furans and dibenzo-dioxins such as 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD). The Los Alamos CAI has the potential for incinerating the treated wood safely while studying the combustion gases and establishing operating conditions which avoid generation of toxic products of incomplete combustion.

As a result of the May 31, 1979 PCB regulations banning the manufacture, distribution in commerce, and use of PCBs, all PCB materials with concentrations greater than 500 ppm must be incinerated under EPA-prescribed conditions. Not only the commercial utility industry but US Department of Energy (DOE) facilities have large quantities of PCBs in use and in storage awaiting treatment methods. For this reason, the DOE has initiated a program at Los Alamos to evaluate PCB incineration in the CAI. Currently, modifications to the existing CAI system are underway to permit the incineration of hazardous liquid wastes such as PCBs and other halogenated organics.

This paper reviews process selection and design criteria which led to the selection and modification of a CAI system for the TRU and hazardous waste program at Los Alamos. The as-built process is described, and operating experience from the experimental program is presented, along with future plans for incineration studies at Los Alamos.

2. PROCESS SELECTION

For TRU-contaminated combustible wastes, the overall incineration process function was to achieve volume reduction and leave an inert residue while assuring no release of contamination to the environment, minimal exposure or hazard to operating personnel, and minimal generation of secondary waste.[1,2] For hazardous or toxic chemical wastes, the same general functions and considerations apply. Anticipated benefits of such processes would include reduced handling and storage hazard potentials; lower packaging, transportation, and storage costs; reduced storage space requirements, and decreased monitoring needs. The necessary generic subsystems are feed preparation and introduction, incineration, offgas treatment, and ash removal and packaging.

For solid wastes, six selection criteria and related performance measures were developed for evaluating candidate processes and process components. Initially the criteria were effectiveness, flexibility, availability, health and safety, resource use, and operability. Considering the project constraint to make maximum use of existing proven technology to develop a volume reduction process, Los Alamos staff selected a controlled-air incineration system with an associated high-energy, aqueous offgas cleaning system. Selection of the aqueous offgas system resulted in the incorporation of an additional subsystem, the scrub liquid recycle system, to minimize secondary waste generation.

More recently, the Los Alamos CAI has undergone further modifications to incorporate the incineration of waste liquids and slurries. These modifications primarily include a waste liquid blending and metering station and a liquid injection burner.

3. PROCESS DESCRIPTION

The Los Alamos CAI process is an assemblage of modified commercially available and custom-designed equipment which has been incorporated into a continuous-system. The more important components of the installation are shown in Fig. 1, a simplified

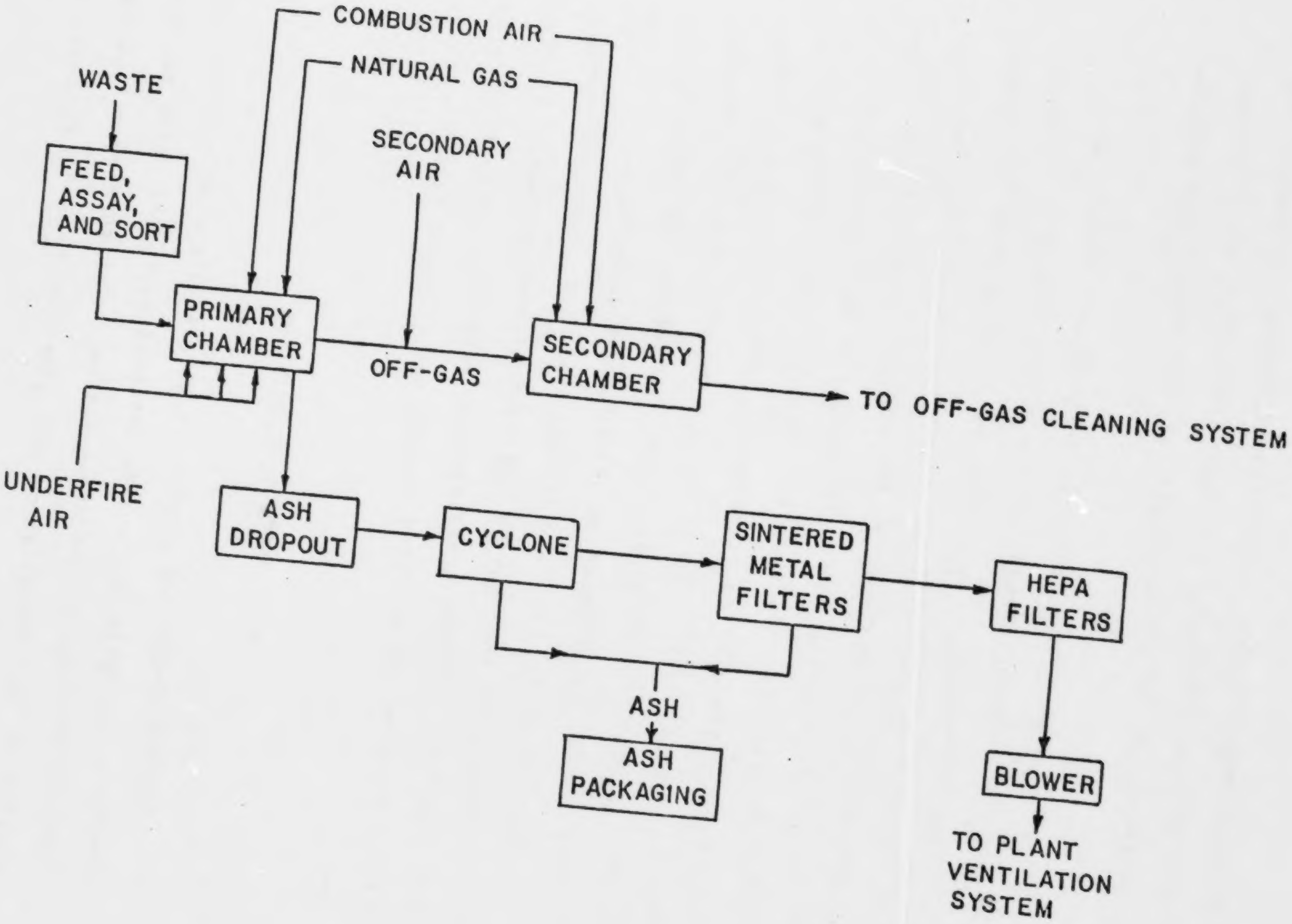

COMBUSTION AIR
NATURAL GAS
WASTE
SECONDARY AIR
FEED, ASSAY, AND SORT
PRIMARY CHAMBER
OFF-GAS
SECONDARY CHAMBER
TO OFF-GAS CLEANING SYSTEM
UNDERFIRE AIR
ASH DROPOUT
CYCLONE
SINTERED METAL FILTERS
HEPA FILTERS
ASH
ASH PACKAGING
BLOWER
TO PLANT VENTILATION SYSTEM

Figure 1. Controlled Air Incinerator Process

flowsheet of the CAI process. There are six subsystems comprising the process: a feed preparation and introduction train for solid wastes, a feed blending and metering station for liquid wastes, a dual chamber incinerator, an offgas cleanup system, a scrub solution recycle system, and an ash removal and packaging system. A brief description of selected equipment and the overall processing sequence for various waste forms is provided in the following paragraphs. More detailed descriptions of individual process components are given in earlier reports.[3,4,5,6]

3.1 Solid Waste Feed System

At Los Alamos, solid TRU wastes are packaged at their source in sealed plastic bags and contained in 0.3 m x 0.3 m x 0.6 m cardboard boxes. The boxes are loaded into the receiving slotbox of the CAI feed preparation line where the packages are assayed for TRU content. Assay is performed using a multiple energy gamma assay system (MEGAS), a nondestructive assay system developed by Los Alamos National Laboratory to analyze for TRU concentrations in low density solids at the 10 nCi/g activity level.[7] The boxes are then passed through an x-ray assembly similar to airport security equipment, which scans for noncombustible materials such as bottles of liquid and large metal objects. Large noncombustibles generally pose no problem from an incineration standpoint, but tend to become stranded on the hearth requiring manual retrieval following a campaign. If necessary, the packages are opened in the sorting glovebox and these items are removed. Following inspection and necessary sorting, the waste packages are transported to the storage glovebox where enough waste is accumulated for about 5 hrs of incinerator operation. During incineration, waste packages are manually transferred from the storage box to the side ram feeder, which in turn loads the main ram feeder in preparation for waste introduction onto the incinerator hearth.

The same general precautions must be followed when preparing highly toxic hazardous solid wastes for incineration. Therefore, the feed preparation and introduction train just described is ideally suited to the handling of hazardous solid wastes. The main function of the feed preparation line is to assure safe and acceptable waste configurations while providing radionuclide or toxic chemical containment and minimizing handling and potential worker exposure to such materials.

3.2 Liquid Waste Feed System

Hazardous organic liquid wastes are received at the facility in properly marked,[8] EPA-approved[9] containers, normally 55-gal drums. The drums are transported on a pallet to the liquid feed system enclosure where the contents are transferred to either of two 155-gal feed tanks. As-received liquid compositions may require some adjustments in heating value, viscosity, or other physical property for compatibility with the feed and incineration systems. This is accomplished typically by blending with No. 2 fuel oil on a batchwise or continuous basis. A simplified schematic of the liquid feed system is shown as Fig. 2.

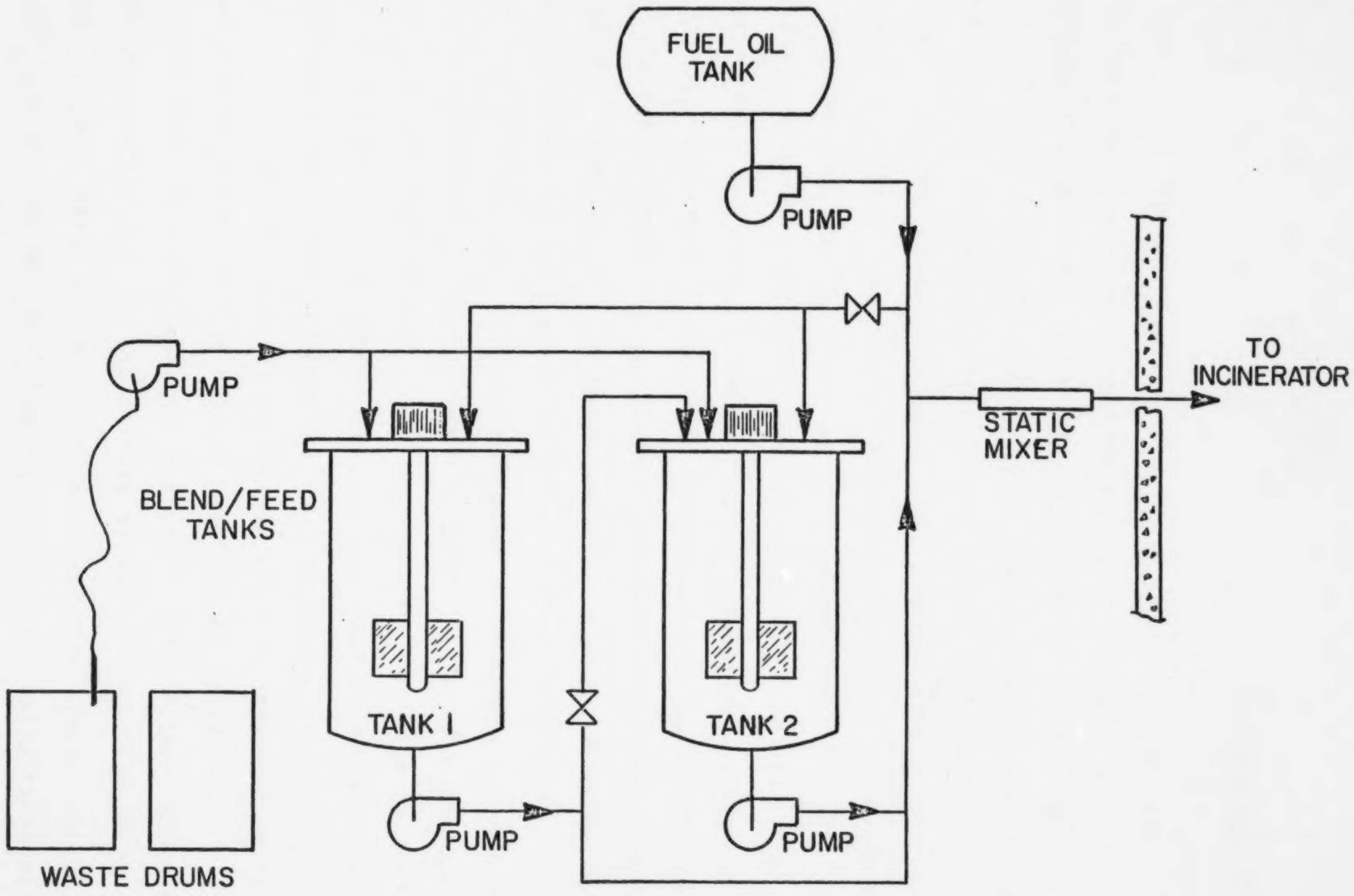

FUEL OIL TANK
PUMP
PUMP
BLEND/FEED TANKS
TANK I
TANK 2
PUMP
PUMP
STATIC MIXER
TO INCINERATOR
WASTE DRUMS

Figure 2. Waste Liquid Feed System

3.3 Incinerator

The incinerator is a conventional dual-chamber controlled-air design (Fig. 3), which has been modified to provide physical containment barriers around the combustion air fans, ash removal doors, and flanged connections to the offgas system ductwork. Similar unmodified models are frequently used for disposal of municipal, pathological, and industrial solid wastes. Both chambers are refractory-lined and natural gas is used for waste ignition and supplemental heat. Solid wastes are charged batchwise via the main ram feeder to the lower chamber where underfire air is used to support combustion under controlled conditions. Unburned volatile components and entrained particles exit the lower chamber through an interconnecting port where excess air is introduced to promote complete combustion. The secondary, or upper, chamber provides the needed residence time for completion of combustion reactions. Supplemental heat is supplied to the secondary chamber as needed. Normal operating temperatures are 870°C in the lower chamber and 1100°C in the upper chamber for TRU-containing wastes, and somewhat higher as required for halogenated organics such as PCBs. Combustion air supply rates are varied depending on waste combustion characteristics.

The original burners were changed to a pre-mix type to allow a higher heat density. Supplementary fuel gas combustion now occurs in the burner block or near it and is less effected by occasional oxygen deficient conditions in the lower chamber. Addition of steam enhances the oxidation of carbon via the water

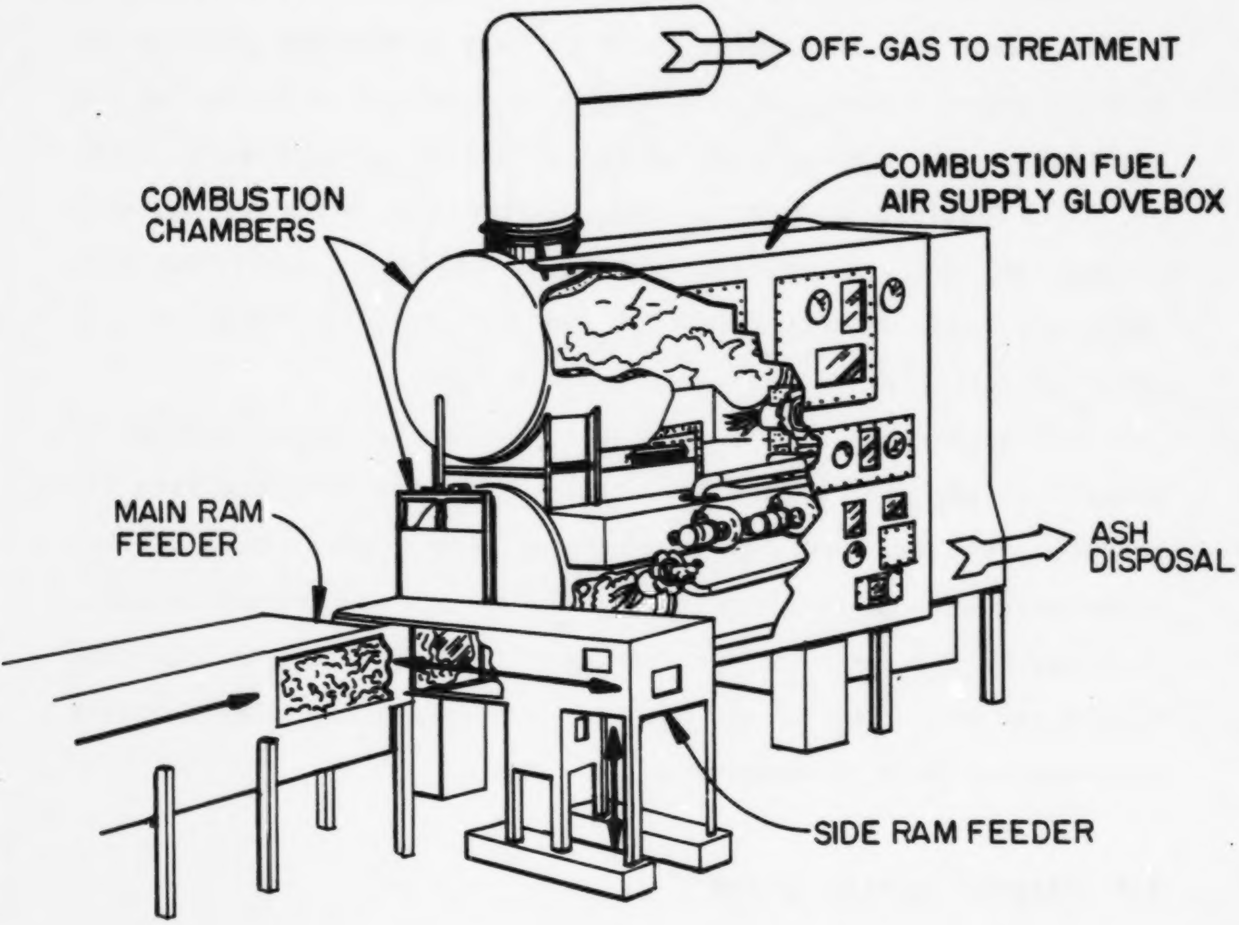

OFF-GAS TO TREATMENT
COMBUSTION FUEL/ AIR SUPPLY GLOVEBOX
COMBUSTION CHAMBERS
MAIN RAM FEEDER
ASH DISPOSAL
SIDE RAM FEEDER

Figure 3. Controlled Air Incinerator Module

gas shift reaction and also favors hydrochloric acid formation which is highly soluble in the scrub solution. Steam is also used as a snuffing medium should a fast shutdown of the process be required. To further promote carbon burnout, the secondary-air injection system was modified to provide more intimate mixing of the excess air with products of partial combustion leaving the lower chamber. More positive oxygen control was achieved by installing oxygen/combustibles analyzers at the exit of each chamber. The analyzers continuously monitor the offgas from each chamber and act to control the level of excess air flow from each; the lower by adjustment of the underfire air flow and the upper by variation of the secondary air flow.

For waste liquid incineration, a commercial vortex burner is mounted on the side of the lower chamber firing directly into the chamber. Waste liquid can be atomized with either steam or air. Combustion air is supplied tangentially into the burner windbox creating high turbulence for thorough mixing of the atomized feed stream and air. The burner has its own natural gas supply should supplemental heat be required.

3.4 Offgas Cleaning System

In addition to the combustion products carbon dioxide and water, exhaust from the CAI upper chamber contains both particulates and mineral acids which result from the combustion of halogenated waste feed streams. Removal of these chemical pollutants and potentially radioactive particulates is accomplished by the offgas cleaning system, which consists of a quench tower, a high-energy venturi scrubber, a packed-column absorber tower, a condenser, a mist eliminator, a reheater, High Efficiency Particulate Air (HEPA) filters, and an activated carbon adsorber. (Fig. 4).

The quench tower is divided into an upper contacting section and a lower separating section. Combustion gases are cooled from the incinerator exit temperature to approximately 70°C by evaporation of recycled scrub solution. Excess solution collects in the separator while the saturated gas phase is routed to the inlet of the venturi scrubber.

The variable-throat venturi scrubber, located between the quench tower and the absorber tower, removes up to 99 wt% of the offgas particulates. The venturi assembly consists of converging and diverging cones with a clamp valve throat to allow the pressure drop to be varied. Venturi pressure drop normally is controlled to 12.45 kPa (50 in. WC). Scrub solution is injected through a nozzle located upstream of the throat. Mineral acids are removed from the gas phase by counter-current contact with process condensate, recycled scrub solution, or fresh water in the packed-column absorber tower.

The condenser, mist eliminator, and reheater are included to condition the process exhaust gases before final HEPA filtration. The condenser lowers offgas temperture, removing the bulk of water vapor from the scrubbed gas stream. The offgas is then reheated to approximately 17°C above saturation temperature to

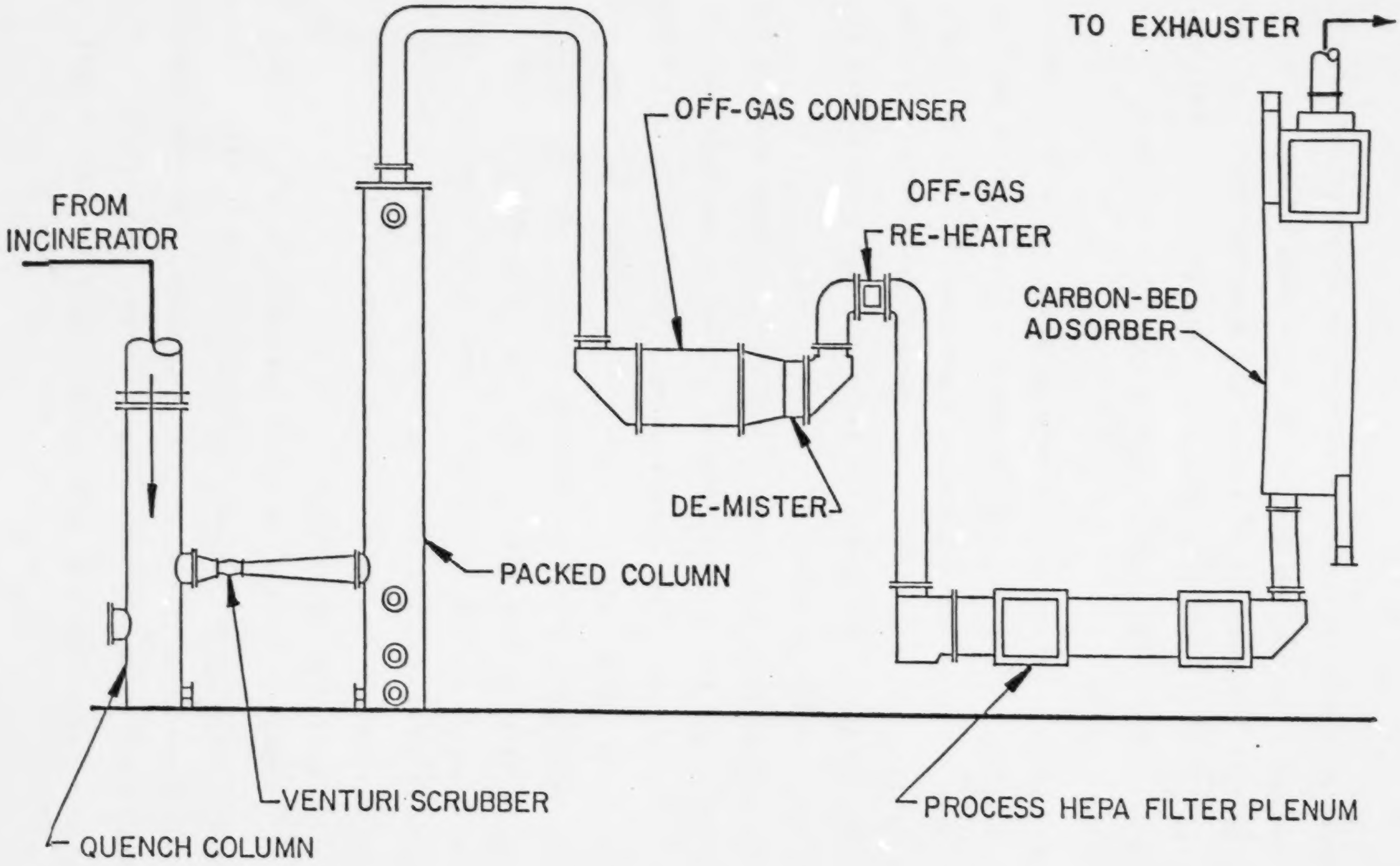

TO EXHAUSTER
OFF-GAS CONDENSER
FROM INCINERATOR
OFF-GAS RE-HEATER
CARBON-BED ADSORBER
DE-MISTER
PACKED COLUMN
VENTURI SCRUBBER
PROCESS HEPA FILTER PLENUM
QUENCH COLUMN

Figure 4. Offgas Cleaning System

avoid condensation and attendant plugging of the HEPA filters and corrosion within the plenum, exit ducting, and offgas blowers. Functional parts of each of these subsystem components are commercial equipment, which are housed in enclosures specifically designed to withstand the 21.22 kPa (85.2 in. WC) pressure differential between this process and ambient conditions.

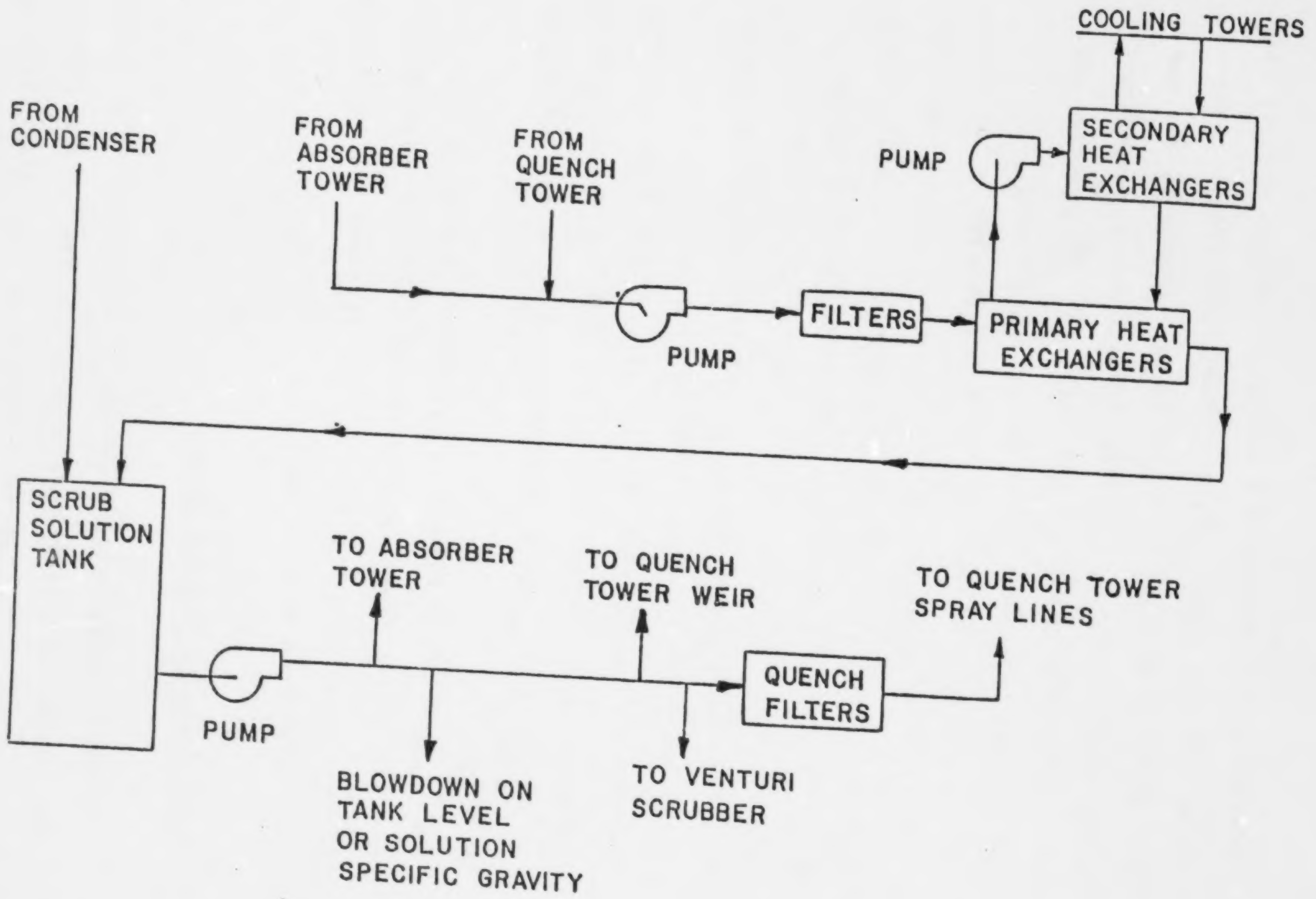
HEPA filtration is required for final removal of particulates. The filter module houses two frames in series; the first consisting of a prefilter and two HEPA filters, the second being similar but without the prefilter. The filter housing is designed to withstand the 20.8 kPa (83.5 in. WC) pressure differential capability of the process and is fitted with hatches to access the bag-out doors and in-place filter testing ports.

The activated carbon bed adsorber serves as a final trap for radioiodine and trace organic compounds. The bed design permits a 0.5 s residence time and a superficial velocity of 15.2 m/s at maximum offgas flow.

The induced draft blower is capable of producing 57.2 kPa (230 in. WC) static pressure absolute at 0.90 m^3/s with a discharge pressure of 78.0 kPa (313 in. WC) absolute (to accomodate the 2255 m elevation at Los Alamos).

3.5 Scrub Solution Recycle System

A scrub solution recycle system is used to minimize liquid blowdown (waste to final treatment) from the offgas cleaning system (Fig. 5). This system consists of full-flow cartridge



COOLING TOWERS
FROM CONDENSER
FROM ABSORBER TOWER
FROM QUENCH TOWER
PUMP
SECONDARY HEAT EXCHANGERS
PUMP
FILTERS
PRIMARY HEAT EXCHANGERS
SCRUB SOLUTION TANK
TO ABSORBER TOWER
TO QUENCH TOWER WEIR
TO QUENCH TOWER SPRAY LINES
PUMP
QUENCH FILTERS
BLOWDOWN ON TANK LEVEL OR SOLUTION SPECIFIC GRAVITY
TO VENTURI SCRUBBER

Figure 5. Scrub Solution Recycle System

liquid filters, a graphite heat exchanger, two evaporative cooling towers, a scrub solution receiver tank, a condensate receiver tank, and a caustic makeup tank. Excess liquid drains from the bottom of the quench tower and combines with scrub solution and venturi blowdown in the packed-column base. This solution is pumped through a 100 μm cartridge filter and a primary heat exchanger to the receiver tank. Liquid requirements for the quench tower, venturi scrubber, and absorber tower are satisfied by recycle from the receiver tank. Solution recycling through the quench tower is refiltered to remove particulates down to 20 μm.

The graphite heat exchanger cools recycled solution from 85°C to 50°C. The process (tube) side is operated at a lower pressure than the coolant (shell) side to guarantee in-leakage in the event of tube failure. The shell side fluid from the primary heat exchanger is cooled by the secondary heat exchange loop, providing isolation from the environment.

To control scrub solution acidity, 20% caustic solution is added at the receiver tank inlet. The addition rate is controlled by a pH sensor on the outlet of the receiver tank.

Condensate from the condenser/mist eliminator drains into a condensate receiver tank. The level in this tank is maintained by addition of fresh water. The solution is then pumped either to the top of the packed-column scrubber or to the receiver tank.

The blowdown rate from the scrub solution receiver tank is controlled by level and specific gravity. If the specific gravity of the scrub solution exceeds a specified value (currently 1.05), or if the tank liquid level becomes excessive, the rate of blowdown sent to the liquid waste treatment plant is increased.

3.6 Process Sampling and Analysis

Sampling and analysis of all major streams during testing operations are essential to evaluate incinerator destruction and combustion efficiencies, evaluate offgas system performance, and to detect and quantify the presence of products of incomplete combustion or recombinant reactions.

The incinerator and offgas system configuration does not permit isokinetic sampling upstream of the quench and scrub system. Gas samples are withdrawn from the hot zone interchamber and from the hot flue gas duct upstream of the quench column. Gas samples are also taken downstream of the HEPA filters and downstream of the activated carbon bed adsorber prior to discharge through the facility stack.

To obtain material balances for hazardous solid waste incineration, solid samples of the feed material and bottom ash are taken to provide data on waste fed to the incinerator and material remaining uncombusted in the ash. Bottom ash samples are collected at the ash packaging station following discharge from the incinerator and transferred to the collection system, providing a homogeneous ash sample from the test run.

Post run samples are collected of filter cake on scrub liquid filters and, if material is present, from the HEPA filters.

On-stream incinerator instrumentation includes gas phase oxygen and combustibles analysis between combustion chambers and at the secondary chamber discharge point. CO and CO_2 analysis of the secondary chamber and absorber tower exhaust streams and final gas flow rate at the HEPA filter plenum discharge are also measured on-line.

Sample analyses are performed within Los Alamos facilities. Gas samples are analyzed by capillary column gas chromatography and high resolution mass spectrometry.

3.7 Ash Removal

Ash generated primarily from the combustion of solid wastes is removed from the CAI by one of two methods. A gravity ash dropout system (GADOS) is used for ash removal during operation and a vacuum ash removal system is used for thorough cleanout of both chambers of the incinerator during shutdowns.

The GADOS consists of a refractory-lined pit and door in the floor of the CAI primary chamber. As new waste is fed to the incinerator, ash is pushed down the hearth until it drops into the ash removal pit. Periodically, the dropout door is opened for a brief time to allow ash to fall through a grate and delumper wheel into a collection hopper. The ash is then pneumatically transferred from the GADOS hopper and collected by a high-energy cyclone and sintered metal filter system into a second hopper for removal at the ash packaging station.

The vacuum system, which is capable of producing up to 26.7 kPa (107.2 in. WC) suction, also is used for vacuum ash cleanout during shutdown. This is achieved by manipulating a vacuum hose in the incinerator chambers through the access doors and gloveboxes on the ends of the chambers.

The ash packaging station consists of a bagout glovebox where ash is removed from the collection hopper through an interlocked isolation chamber. The chamber is first opened to the ash hopper and allowed to fill and is then isolated from the hopper and opened to drop contents into a collection bag.

After the ash is packaged it is stored for future studies or immobilization processing.

3.8 Control and Instrumentation

Design and specification of the CAI process control system received priority attention throughout the planning and construction phase. As the "nerve center" for the process, the controls not only assure effective component performance, but monitor performance data to assure the safety of continuing operations. Control design considerations started with the parameters affecting operation of the incinerator and primary offgas components. As the process design evolved, the considerations broadened to encompass the operation of ancillary equipment including backup utility supplies. A detailed description of the complete control system is well beyond the scope of this paper, however, the incinerator control features and a general overview of the total system design are described below.

Controls on the as-received incinerator were largely limited to pre-set conditions based on combustion experience for a particular waste composition. These controls were upgraded to accept a wider range of feed compositions and to minimize thermal cycling in the lower chamber. Both air and natural gas supplies are modulated to permit proportional rather than step response to demand. The air introduction rate for each stage is controlled by feedback from oxygen analyzers located at the exit of each chamber. The pressure differential between the incinerator interior and the operating area is maintained by a valve immediately upstream of the induced draft fan. Flow measuring elements and recorders monitor air, natural gas, and steam introduction rates for energy and material balance purposes.

For the offgas cleanup, conditioning, and filtration equipment downstream of the incinerator, the controlled variables are: venturi scrubber liquid feed rate and pressure drop; absorber tower liquid feed rate; condenser gas-phase temperature decrease; reheater gas-phase temperature increase; and HEPA filter pressure drop. The pressure drop and nominal temperature of each component is also monitored as an indication of normal vs. deteriorating performance.

In the scrub solution recycle subsystem, a pH feedback arrangement controls neutralization of the liquid effluent from the primary offgas scrubbing components. Differential pressure is monitored across each liquid filter; process side temperatures are controlled in the graphite heat exchanger. Liquid level and specific gravity are controlled in the scrub solution receiver tank.

The primary variables as well as many other secondary variables and parameters are controlled and/or recorded at a central station. Variables considered critical to process operation and safety are tied into an alarm panel which positively identifies the off-range variable as an aid to trouble shooting. Off-range variables identified as vital to process safety will activate one of two automatic shutdown modes -- controlled or fast. Less critical variables require only operator response to correct off-range behavior.

A data acquisition system automatically records additional variable and parameter values generated during experimental CAI process runs.

3.9 Auxiliary Equipment

Backup utilities provide required services for an orderly process shutdown under abnormal circumstances. A diesel-powered generator, kept running during all incinerator operations, supplies standby power to high consumption equipment and vital motor-driven equipment. An on-line, floating battery system provides electrical power for process controls, data collection, and averting potential momentary power interruptions, which could result in control relay dropout. A two-hour auxiliary cooling water supply is stored in a pressurized container for release to the quenching system in the event of a recirculation pump failure because loss of cooling water constitutes an immediate threat of damage to process equipment. A backup air compressor and compressed nitrogen are available to supplement normal instrument air supply if required. Pneumatic actuators are designed to "fail safe" on loss of air pressure. Snuffing steam is injected into the primary chamber to extinguish burning waste in the event of a fast shutdown at high temperature to prevent uncontrolled burning and inefficient combustion, which can clog the offgas cleaning system with soot and heavy tars.

Radioisotope containment for the building is maintained by physical barriers and zoned ventilation. There are four separate ventilation zones. The pressure in each zone is regulated so that ventiliation air moves from the highest pressure zone (atmospheric) toward the lowest pressure zone (the volume internal to the process). The interface between each zone is controlled by physical enclosures. The zone ventilation system is shown in Fig. 6.

4. EXPERIMENTAL PROGRAM AND RESULTS

The CAI experimental program at Los Alamos is divided broadly into two areas by waste classification: radioactive and hazardous. All experimental work to date has been directed toward incineration of radioactive solid wastes. This work consisted of two phases. Phase I involved cold (nonradioactive) testing and development completed in late 1979, and Phase II was a hot (radioactive) testing and demonstration which was completed in May 1980. Since the completion of Phase II, modifications to

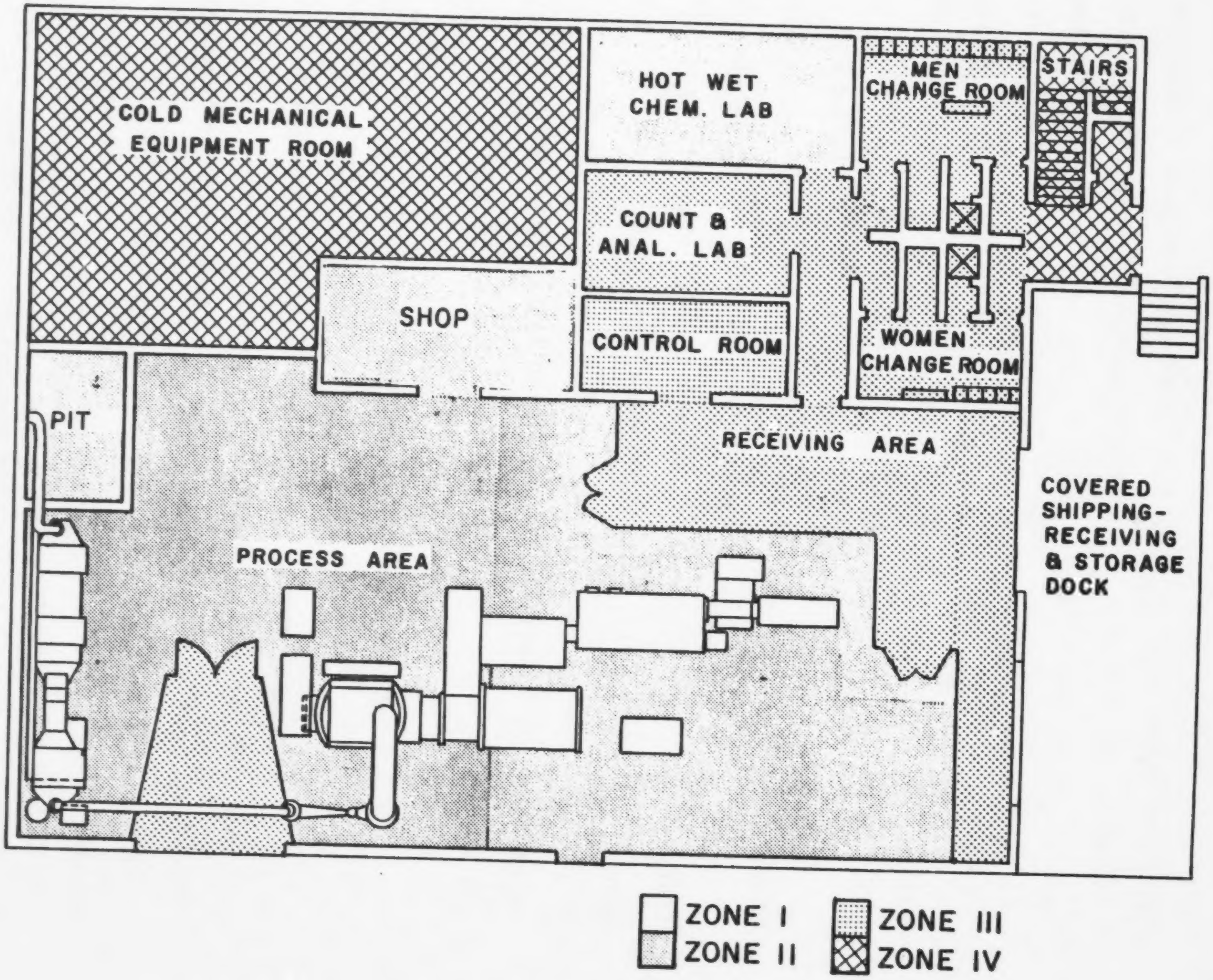

COLD MECHANICAL EQUIPMENT ROOM
HOT WET CHEM. LAB
MEN CHANGE ROOM
STAIRS
COUNT & ANAL. LAB
SHOP
CONTROL ROOM
WOMEN CHANGE ROOM
PIT
RECEIVING AREA
COVERED SHIPPING-RECEIVING & STORAGE DOCK
PROCESS AREA
ZONE I
ZONE II
ZONE III
ZONE IV

Figure 6. Building Ventilation for Radionuclide Containment

the existing system have been underway to incorporate hazardous solid and liquid wastes into the CAI development program.

4.1 Cold Testing and Development

The cold testing and development phase consisted of an initial equipment checkout period followed by six runs using non-contaminated waste materials. During the initial checkout, the incinerator module was operated for about 500 hrs in the as-received configuration. Operating experience and data obtained during the checkout were applied in design of process modifications for radioactive service.

A series of six nonradioactive test runs were made to check out the various subsystems and to establish operating parameters, identify additional modification requirements, and evaluate safety and containment aspects of the process. Phase I was a continuing effort to evaluate, modify, and re-evaluate equipment performance resulting in a process with improved operability, containment, and effectiveness.

A cold test run designed to check out process operation at design feed rate was made using high plastics containing wastes. Individual waste compositions for this run included various cellulosic materials with up to 50% PVC, 50% polyethelene, and 20% latex.

Performance of the CAI improved steadily throughout the cold testing and development phase. Significant results included 1) attainment of designed throughput while incinerating design basis feed, 2) successful operation of all associated subsystems, 3) highly effective offgas cleanup resulting in chloride and sulfate concentrations in the condensate of less than 8 ppm and 10 ppm, respectively, and 4) long HEPA filter life with one set in use in excess of 230 hrs.

4.2 Hot Testing and Demonstration

Following successful completion of the cold testing and development phase, two hot test runs were completed using actual TRU-contaminated waste. The total time during which waste was fed to the incinerator was approximately 38 hrs. The first run (Run #7) was made using suspect TRU-waste consisting of room trash from the Los Alamos Plutonium Processing Facility. Secondary wastes such as liquid cartridge filters, surgeons gloves, and other suspect room trash generated during the run, were also incinerated. A total of 15.4 kg of noncombustible materials were identified in the x-ray scan and removed in the sorting operation.

CAI Run #8 was a TRU demonstration run of design basis feed composition containing an average of 20 nCi/g of ^{239}Pu plus ^{241}Am. The incinerator was operated at feed rates of 27.2 and 45 kg/hr during the run. Both runs were highly successful operationally with total radionuclide containment. Ash removal and packaging operations were successful and the offgas system performed as expected with no significant deterioration of the final HEPA filters observed during either of the runs. Operational data for each CAI TRU-waste test run are summarized in Table 1.

TABLE 1

CAI TRU-Waste Test Run Summary

	Waste Feed	Total Waste		Reduction Factor	
Run #	**Duration, Hrs**	**Weight,kg**	**Volume,m^3**	**Volume**	**Weight**
7	17	213	3.68	130:1	29:1
8	21	272	3.40	120:1	40:1

4.3 Documentation and Technology Transfer

A major current effort in the CAI development and demonstration project is the preparation of detailed design and operating documentation for the system. Technology transfer to other Department of Energy contractor sites and to the commercial sector has been a continuing effort and will be emphasized in the future.

The documentation task will provide all information required for an interested user to duplicate the process including equipment specifications, drawings, calculations, and suggested modifications. Experimental results, operating procedures, and the final safety analysis will be published separately. The complete package should be available in late 1981.

4.4 Future Plans

With a major effort presently underway to evaluate and demonstrate the applicability of the Los Alamos CAI to incineration of hazardous solid and liquid wastes, technology transfer will receive major emphasis in this area as well.

Beyond incineration of TRU-containing and hazardous wastes, the CAI process appears applicable for volume reduction of low activity level fission product wastes. However, the behavior of volatile and semi-volatile fission product species through incineration systems has not been addressed. Tracer level studies to determine the fate of ruthenium, cesium, cobalt, iodine, and iron will begin this year.

5. SUMMARY

Modification of commercially available equipment and technology for radioactive service and production scale incineration of TRU-contaminated wastes were successfully demonstrated. Further modifications are presently underway to incorporate incineration studies of hazardous solid and liquid wastes into the Los Alamos CAI development program. Additional current efforts include documentation of the CAI process design, operating procedures, and process data generated during the experimental campaigns. Technology transfer has and will remain an important object of the program.

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SESSION 3

TECHNOLOGY SYMPOSIUM I

CHAIRMAN:

J. E. Thibault, Jr.
J. E. Thibault & Associates
Providence, RI

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EXPERIENCE WITH THE CINCINNATI MSD HAZARDOUS WASTE INCINERATOR

J. H. TRAPP
Metropolitan Sewer District of Greater Cincinnati
Cincinnati, OH

B. T. RILEY, Jr.
Rycon, Inc.
Cincinnati, OH

ABSTRACT

The MSD of Cincinnati and Hamilton County, Ohio operates a hazardous waste incinerator system. This system consists of a rotary kiln and processing line for solids, and a tank farm and cyclonic type combustion chamber for liquids. A system description is presented, along with a comparison of design and operating experience.

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The MSD serving Cincinnati and Hamilton County, Ohio and associated municipalities surveyed the sources and rates of industrial waste generation in its service area in the late 1960's and early 1970's and determined a need for an industrial (hazardous) waste incinerator. A design was commissioned and the incinerator operations were initiated in 1979. Since that time, during intermittent periods of operation, more than a million gallons of various industrial wastes have been satisfactorily incinerated.

The original design goals of the incinerator emphasized three basic capabilities.

1. To accept and incinerate grit from primary grit chambers and shredded bar screenings produced by the adjoining 120 MGD sewage treatment plant.
2. To accept and incinerate skimmings from primary settling tanks.
3. To accept, store, mix, stage and burn wastes from local industrial sources.

The incinerator was constructed on the premises of the Millcreek Sewage Treatment Plant, located in the Lower Price Hill area of downtown Cincinnati. The sewage treatment plant includes primary settling and conventional activated sludge treatment facilities. Sludge is treated in sludge digestors to produce methane which fuels a stationary electrical generating plant of 4 megawatt capacity. Digested sludge is disposed of by multiple hearth incinerators.

DESCRIPTION OF THE SYSTEM

Wastes are most commonly delivered by tanker truck from a variety of sources to the receiving station of the incinerator complex. The waste is pumped from the truck through pre-strainers whose round hole openings may be varied from 1/8" to 3/8" openings according to information available on the waste. Selection of the screen is dependent on the viscosity of the material and the known solids content provided by waste acceptance procedures. The wastes are pumped by one or more of four pumps to a holding tank for placement in selected storage tanks in the tank field.

A small drum unloading and discharge facility is available for the management of drummed wastes, although the delivery of drummed wastes is not encouraged by the facility. An elevated unloading dock is provided for the removal of drums from trucks and a drum tilt and discharge mechanism into a sump from which wastes are pumped to a holding tank is provided.

From the unloading point, the wastes may be delivered either to the 6,000 gallon holding tanks for mixing or directly to selected storage tanks of 25,000 gallon capacity. The tank farm includes four 6,000 gallon preliminary holding tanks and ten 25,000 gallon storage tanks, four 12,000 gallon storage tanks, and an additional 25,000 gallon uninsulated tank for fuel oil storage to service the facility.

The entire tank farm is housed on a concrete apron with a concrete spillwall and trench drain which is valved to prevent spills but will allow the removal of rainwater. Drainage from the farm is directed to the inlet of the sewage treatment plant or returned to one or more storage tanks. Each waste storage tank is insulated and was originally designed with internal steam heating coils of the suction type. Due to corrosion problems associated with the heating coils and caking of the waste on the coils, which negated their heating efficiency, the heat exchangers in the waste storage tanks were removed. When necessary, wastes are heated by operating the 40 HP mixer until suitable temperatures and viscosities are achieved. A differential pressure transducer is mounted on the base of each tank to provide continuous digital read-outs at the control panel. Tanks are also monitored, in addition to weight, with a volume gauge located in the control room. In general, the tanks in the tank farm are clustered in groups of two or three and each group is served by two or more pumps which may be operated separately or concurrently to remove wastes from the tank or to add wastes to the tank. Under normal operating conditions, two of the ten storage tanks are planned to be used for storage of skimmings from clarifiers and primary settling tanks at the municipal sewage treatment plant.

The total diked containment capacity is approximately 650,000 gallons. Total tank farm capacity including holding tanks, storage tanks, fuel oil storage, etc. is approximately 460,000 gallons, leaving approximately a one and one-half foot freeboard in the event of a catastrophic spill. A complete foamite fire protection system is installed throughout the tank farm. In addition, each tank is overlaid with nitrogen to reduce the possibility of oxidation, polymerization or spontaneous combustion events occurring while waste is stored, loaded, or unloaded.

During incinerator operation, the wastes are removed from the storage tanks and combined in one or more of four batching tanks. Wastes are blended according to chemical compatibility and heat content and, thus, provide a relatively uniform fuel value to the combustion systems. A target of 7,500 BTU's per pound is used for blending schedules. The tanks are flat bottom in design and are not washed between different waste charges. To date, no difficulties have been encountered with reactions between waste residues in the tanks and new wastes.

The blended wastes are removed from the batching tanks and delivered to either of two combustion systems. One is a rotary kiln combustion system with the capability of burning liquid wastes in addition to certain types of granular solid materials. The second is a liquid injection combustion chamber. Both of these primary combustion chambers discharge into a secondary combustion chamber.

Table I describes the design capacities of the rotary kiln, the liquid injection combustor and the secondary combustion chamber.

Table I Equipment	Volumetric Capacity gal/hr	Maximum Heat Release MMBtu/hr	Maximum Temperature °F	Minimum Residence Time/sec
Kiln	1200	65	2400	0.1
Cyclone	1200	77	3100	0.1
Combustion Chamber	N/A	N/A	2500	1.0

Liquid wastes are delivered by heat-traced, insulated pipelines from the batching tanks to externally atomized type nozzles in both the rotary kiln and the liquid injection combustion chamber. Atomization was originally provided at these nozzles with steam; however, high steam demand in other operations of the waste water treatment plant created a need to temporarily use compressed air as the atomizing agent. Air is being supplied by portable rotary air compressors pending installation of new boilers. In addition, compressed air is used to operate all controls in both the tank farm and combustion facilities.

A solids handling system available at the plant has two distinct capabilities. The first is an in-ground hopper for receiving grit by dump truck delivered by the municipal sewage treatment plant. It consists basically of three receiving chambers of approximately eight cubic yards capacity from which solids are removed by screw conveyor and fed to a bucket elevator. The bucket elevator delivers the solids to a lateral conveyor which delivers the material to the gravity feed chute of the rotary kiln. This system could be used for contaminated combustible solids that are finely divided, e.g., PCB-contaminated soil.

Bulky solids may also be handled by the system. A single truck discharge hopper is provided to receive oversize material which is conveyed by a steel plate conveyor to a 150 HP Eidal shredder. The output from the shredder is carried by belt conveyor to the bucket elevator which lifts the material to the discharge point of the rotary kiln. Neither solids handling system is capable of accepting semi-solid material at the present time. In addition, due to the open handling system, solids contaminated with extremely volatile or powdery materials cannot be accepted because of the danger of excessive fugitive emissions from the system. The design could be modified to accept these materials should a waste generator require this type of service.

The rotary kiln combustion chamber is approximately 20 feet in length and 12 feet outside diameter. Inside diameter and length of the kiln are 10 feet and 20 feet. The injection combustion chamber is approximately six feet in diameter and 11 feet in length. The secondary combustion chamber is vertically oriented with hot gases entering the base and leaving the top of the chamber. It is cylindrical, approximately 13 feet 6 inches in diameter by 40 feet in height, and surmounted by an emergency stack bypass for use when power or scrubber water is lost. The three combustion chambers are constructed of carbon steel, ASTM A-283, and lined with refractory and insulating brick. Maximum operating temperatures are 3100° F in the liquid injection chamber, 2400° F in the kiln, and 2500° F in the combustion chamber exit. Ash and slag are removed in a quench tank and transported via pipeline to a holding lagoon located near the incinerator.

The hot gas flows from the secondary combustion chamber into a horizontal duct where quench water sprays reduce the temperature of the gas stream to less than 1000° F. Thence, they pass into a vertically oriented variable throat venturi scrubber where recirculated water is added to remove particulate matter. The duct work and venturi scrubber are lined with silicon carbide block, while the shell is constructed of Corten (ASTM A-242). The gas stream turns 90 degrees and enters the base of an acid neutralization scrubber. This absorber is vertically oriented, approximately 15 feet in diameter and 30 feet tall, and is of the sieve tray type. Its function is to neutralize acid gases. The scrubber shell is lined with glass flake polyester to minimize corrosion. The trays are 316 stainless steel. Absorber water is supplied from the principal blowdown tank after pH adjustment with 50% caustic (sodium hydroxide) from two standby 10,000 gallon storage tanks. The cooled, neutralized gas flow exits the top of the scrubber and is conducted vertically down to an induced draft fan powered by a 1500 HP motor. The fan housing is lined with rubber and the fan blades are constructed of Inconel 625. Gases exiting the induced draft blower pass into a seven foot diameter stack approximately 90 feet in height and constructed of cylindrical sections of 3/16 inch stainless steel. Three pumps are used to supply water to the quench system and to the venturi scrubber. Two are used to recirculate flow from the blowdown tank to the neutralization scrubber. An emergency water supply mounted on a vertical tower approximately 120 feet in height is designed to supply quench water to the system should pumping capabilities or power be lost to the system. Quench water is supplied for five minutes of operation which is sufficient to allow shutdown of the system and opening of the emergency cap.

After the complete scrubbing system, gas exits at approximately 180° F; emissions are designed to be a maximum of .03 grains per standard cubic foot at 70° F and 12% CO_2. Emission tests have indicated that acid emissions have been completely neutralized, <2 ppm HCl, but that particulate emissions, while within state limits, are about .08 grains per DSCF. Better quenching, to $<200^\circ$F, should allow achieving the design rate.

A major design change in the facility was the installation of sound suppression devices in the stack. Due to the nearness of luxury apartments, several complaints were received concerning the level of sound. Modification of the stack to incorporate sound suppression devices has eliminated the complaints and lowered the noise level by 20+ decibels.

Process control and operation is carried out in a centrally located building housing the main control panel. The control panel offers complete monitoring of both the tank farm and the combustion facilities. The tanks are monitored for both valve position, i.e., in-flow, out-flow, non-operation, liquid level, and weight of tanks. Pump motors are indicated to be in an on-off position and valve openings are displayed. Digital read-outs are provided for waste temperatures in each tank. On the combustion system, temperatures are monitored both by drum type direct reading gauge and continuous recorder as well as digital temperature read-out. Temperature monitoring points are at the exits of the rotary kiln and cyclone and at the exit of the secondary combustion chamber. Overall system control is exercised based on the BTU content of the waste to be burned. Waste flow is automatically varied to maintain set point temperatures. Also automatically controlled are negative draft in the combustion chamber (about 1-1/2 inch water), venturi pressure drop (28" - 30" water), and pH of recirculated water exiting the absorber (6.5 - 7.0).

A broad variety of liquid wastes can be burned in the incinerator system. Reasonable quantities of bulky solids may be burned after shredding and granular wastes can be incinerated. A general category of wastes which are currently excluded from the incinerator is semi-solid material that is too viscous to be handled as a pumpable fluid but too sticky to be handled in a dry solids handling system, such as the bucket elevators and conveyor represent. Should a demand for this type of service be sufficiently great, equipment could be added to the system which would allow its combustion.

The waste acceptance procedure in general is as follows. The waste generator contacts the facility, furnishes a sample and a detailed analysis which must include lead, mercury and sulfur. This information is reported on a Customer Representation Sheet. Prohibited materials include radioactives, explosives, PCB's except as permitted, pesticides pending a test burn, and Group IA and IIA metals. Critical considerations are BTU content, acid value, water content, flashpoint, viscosity, and settleable solids. If the sample is determined to be compatible with facility capabilities, arrangements are made for delivery of the waste load by tanker truck. On arrival of the tanker, a sample is drawn and subjected to infrared analysis. If its analysis matches that of the preshipment sample, the waste is pumped into a receiving tank. Facility laboratories analyze this waste for the following items: heating value, total halide, acid value of products of combustion, ash content, water content, specific gravity, and pH. A principal area of difficulty encountered to date has been the poor sampling technique used by waste generators or haulers. Too often a waste is represented as having a high BTU content because a poor sample has been taken. On delivery and sampling, it is discovered that the waste load is mostly water.

TYPICAL WASTES WHICH HAVE BEEN BURNED BY THE FACILITY

In excess of one million gallons of a broad variety of wastes have been burned by the facility since it was placed into operation. Typical of these are the following types of materials.

1. Paint manufacturing wastes. The principal components of this waste include titanium dioxide, talc, paint resins and organic solvents of a wide variety. The flashpoint of the waste is below 80° F. Typical water content is 13%, settleable solids content of approximately 10%, a pH of 7.7, and a single liquid phase. This waste contains about 84 ppm of lead, 0.17 ppm of mercury, and 0.1% sulfur. Heat content of the waste is approximately

11,000 BTU's per pound.

2. Methyl methacrylate wastes are produced in recovering methyl methacrylate from polymethyl methacrylate products such as plexiglas.$^{(R)}$ They typically are composed of water, methyl methacrylate 10%, various solvents 5%, lead 2.9%, mercury <0.5 ppm, sulfur 0.079%, chlorine .15%, and phosphorus .26%. Heat content of this waste has average 11,000 BTU per pound.

3. Ink waste. A typical waste seen intermittently by the facility is the waste produced in the manufacture of various types of printing ink. The waste consists predominantly of cellosolve, normal propyl alcohol, ethyl acetate, ethyl alcohol, normal propyl acetate, and isopropyl alcohol, plus water. The lead content is about 1.2 parts per million, mercury is less than .005 ppm, and sulfur is approximately .04%. Average heat content is about 12,000 BTU's per pound.

4. Spent solvent mixtures. These are generated by a number of specialty chemical manufacturers in the area. A typical one might consist of ethylene dichloride mixed with acetic acid with a heat content of approximately 6,000 BTU's per pound, having a nitrogen content of .25%, a chlorine content of 36%, a sulfur content of .02%, a mercury content of 0.1 mg. per liter, a lead content of .02%, and a flashpoint of less than 73° F.

5. Specialty chemical manufacturing residues. These wastes

often represent a compilation of many drums of residues left over from various different chemical production areas. Very often the drums are combined into a tanker load of 1200 to 1500 gallons. A typical waste might have a heat content of about 10,000 or more BTU's per pound, a sulfur content of under 0.25%, mercury content of <0.01 ppm, lead content of 0.8 ppm percent, a chloride content of approximately 5% to 32%, an alcohol content of 10% to 15%, and a chlorinated hydrocarbon content of 10% to 40%.

6. The incinerator has already received extensive quantities (Several hundred thousand gallons) of waste being removed from abandoned industrial waste sites. The analyses available on these wastes are extensive since MSD requires an analysis for the 129 priority pollutants according to the U.S. EPA protocol. The analysis of a specific waste indicated the presence of 14 heavy metals (in the ppm range), cyanide (ppm), approximately 16 volatile organics such as benzene (3%) and toluene (5%), phenol (1%) from the acid fraction and several different compounds from the base/neutral fraction. No pesticides were detected. A trace amount of kepone was found. The pH of the waste as agglomerated was 6.5 to 7.5 with two liquid phases. Heat content of the waste was approximately 6,000 BTU's per pound as received.

FUTURE PLANS

In general, the operating experience of the facility has been satisfactory. Additional equipment is being installed to enable the incinerator to accept and destroy PCB type wastes or PCB containing wastes. A dedicated station to receive high pour point wastes is also contemplated. One problem faced by the facility to date has been a general lack of wastes on a continuous or consistent basis. The incinerator has operated on an average about four months per year for the last two years, burning 10,000 to 14,000 gallons of waste per day. A stepped-up marketing effort is expected to remedy this condition. Additional wastes would be welcomed by the facility in order to increase on stream factor to approximately 80 to 90% and throughput to about 25,000 gallons per day.

SHIPBOARD AT-SEA INCINERATION OF HAZARDOUS CHEMICAL WASTES

R. J. JOHNSON and P. J. WELLER
TRW, Inc.
Redondo Beach, CA

L. A. MARTINEZ
Maritime Administration
Washington, DC

D. A. OBERACKER
U. S. Environmental Protection Agency
Cincinnati, OH

M. L. NEIGHBORS
Diversified Maritime Services, Inc.
Washington, DC

ABSTRACT

This engineering study assesses the key aspects of at-sea incineration of hazardous chemical wastes, including the total shipboard incineration system, conceptual vessel designs, and waterfront facility requirements. Preliminary evaluation of generic incinerator types potentially applicable to shipboard operation resulted in the selection of liquid injection incinerators for destruction of pumpable wastes. A rotary kiln is recommended for shipboard experimental evaluation of solid hazardous waste incineration. The vessel conceptual design study presents two new ship alternatives, each of approximately 8,000 metric tons waste capacity and equipped with three liquid injection incinerators and one rotary kiln. Requirements are described for a dedicated waterfront support facility to receive, store, and blend or process wastes prior to loading onboard incinerator vessels. A review of existing U.S. terminal facilities identified 139 ports and 1,221 terminal docks, piers or wharves on the East, Gulf, and West coasts of the continental U.S. that have sufficient water depth and space to receive the conceptual design incinerator ship. A U.S. incinerator ship is recommended as an effective means of disposing of hazardous materials and conducting incineration research in a location minimizing the risk to public health and the environment.

INTRODUCTION

The serious environmental and public health concerns associated with hazardous waste disposal in the United States have prompted various federal agencies to examine alternate technologies for treatment and destruction of these materials. High temperature incineration, whether on land or at sea, is the most effective method available today for the destruction of combustible hazardous wastes, e.g., toxic organochlorines, typically destroying 99.99 percent of the wastes. Incineration at sea removes the destruction site from populated areas and the vulnerable freshwater environment, which is of special importance when incinerating the most toxic wastes.

Several foreign flag incinerator ships have been operating in Western Europe for about a decade. In 1974, 1975, and 1977, three officially sanctioned at-sea incineration operations were successfully conducted in the United States aboard one of these foreign incineration ships, the M/T Vulcanus.* Eight shiploads of industrial organochlorine wastes were incinerated in the Gulf of Mexico and three shiploads of Air Force Herbicide Orange were destroyed near Johnston Island in the Pacific Ocean under research and special permits issued by the Environmental Protection Agency. These operations and those in Europe have demonstrated that incineration at sea of liquid combustible chemical wastes is an industrial operation which is available now and which can be implemented without much of the preliminary testing that other ultimate disposal alternatives may require.

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* The M/T Vulcanus was purchased by Waste Management, Inc., a U. S. firm, in 1980.

In February 1980, an interagency work group* undertook a study of at-sea incineration technology and the various alternatives available to the Federal Government for the design, construction, and operation of U.S. flag incinerator ships. The study examined previous incineration operations, various federal assistance programs, safety and control measures, conceptual designs for incinerator ships, environmental impacts, and waterfront facilities. In September 1980, the work group issued its report.[+] It concluded that chemical waste incineration at sea aboard specially designed and equipped ships is a cost-effective, technically efficient, and environmentally acceptable technology for the destruction of many types of combustible hazardous waste.

SHIPBOARD INCINERATION SYSTEM

All currently operating incineration ships are limited to destruction of homogeneous pumpable liquid wastes. The U.S. Environmental Protection Agency has recommended that a U.S. flag incinerator ship be designed and constructed not only to dispose of the accumulation of hazardous materials by present state-of-the-art technology but also to extend the capabilities of at-sea incineration to include destruction of solid materials. An engineering evaluation was conducted of potential incineration systems capable of destroying solid as well as liquid wastes.[++]

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* Membership included the U.S. Environmental Protection Agency; U.S. Department of Commerce, Maritime Administration; U.S. Department of Transportation, Coast Guard; and U.S. Department of Commerce, National Bureau of Standards.

[+] "Report of the Interagency Ad Hoc Work Group for the Chemical Waste Incinerator Ship Program", September 1980.

[++] Johnson, R.J., et al., "Design Recommendations for a Shipboard At-Sea Hazardous Waste Incineration System", Appendix B to above interagency report.

Candidate Incinerator Types

Major characteristics of candidate types of incinerator assessed for shipboard at-sea application are compared in Table 1. Capability of each incinerator to destroy different types of waste material is noted in the table, along with maximum operating temperature, relative maintenance requirements, and present commercial applications.

The liquid injection incinerator can be used only for pumpable liquids; however, it is the most effective means of incinerating liquid wastes at high feed rates and is capable of attaining the temperature required (up to 1600^{0}C) for highly efficient destruction of toxic materials. It can also serve as an afterburner for a solid waste incinerator. Maintenance of this type of incinerator is low because there are no moving parts within the high temperature zone. Liquid injection incinerators are widely used in commercial applications and represent the only technology well proven for at-sea destruction of harzardous wastes.

Rotary kilns are the most versatile incinerators available, capable of handling any combination of liquids, slurries, tars, or solids. Temperatures as high as 1400^{0}C can be attained. Rotary kilns represent well proven technology for land-based incineration; however, their use at sea would be a new application. Specially designed equipment will be required to withstand pitch, roll, vibration, and environmental conditions at sea. Maintenance may be higher than for a liquid injection system. A rotary kiln coupled with a liquid injection incinerator is considered to be the most versatile system for thermal destruction of a wide variety of hazardous wastes.

TABLE 1. COMPARISON OF CANDIDATE INCINERATOR TYPES FOR SHIPBOARD AT-SEA APPLICATION

	Liquid Injection	Rotary Kiln	Fluidized Bed	Molten Salt	Multiple Hearth	Multiple Chamber
Waste Types						
Pumpable liquids	x	x	x	x	x	x
Slurries, sludges		x	x	x	x	
Tars		x		x	x	
Solids						
granular		x	x	x	x	
irregular		x				x
containerized		x				x
Maximum Operating Temperature, °C	1600	1400	980	980	1100	1000
Maintenance	low(a)	med(a,b)	med(a,c)	med(a,d)	high(e)	med(e)
Applications	widely used,(f) liquid wastes	widely used, all wastes	limited use, sludges and organics wastes	demonstration tests only	widely used, sewage sludge	widely used, refuse

(a) No moving parts in high temperature zone

(b) Bearing and seal modifications required

(c) Ash removal and bed replacement required

(d) Salt recycle or replacement required

(e) Moving parts in high temperature zone

(f) Liquid injection incinerators are the only type that have been successfully utilized for shipboard at-sea operation

Fluidized bed incinerators are more limited than rotary kilns in the range of feed materials accepted (Table 1) and are not suited for irregular solids or tarry substances. Maximum operating temperatures are typically limited to 980°C to avoid fusion of the silica sand bed material. Higher temperatures of 1200°C are possible using alumina refractory particles as the bed material. Maintenance includes ash removal and replacement of the bed when necessary. Pitch and roll of the ship, particularly during storms, would cause shifting of the large mass of bed material both during incineration and when shut down.

Molten salt reactor pilot and demonstration units have been used to destroy liquid, slurry, and granular solid waste materials; however, no large commercial units are presently in operation. Operating temperature of the salt bed is typically limited to 980°C. Pitch and roll of the ship will cause sloshing of the molten salt within the reactor. A potential advantage of this sytem is that it can serve as a combined incinerator/scrubber by retaining particulates and contaminants in the bed; however, this necessitates salt regeneration or replacement. The salt bed must also be removed from the reactor before solidification during shutdown. A spill of the hot, caustic salt containing toxic contaminants could pose hazards aboard ship.

Multiple hearth incinerators are widely used for sewage sludge disposal, but can also accept granular solids and liquids (injected through auxiliary fuel nozzles). Operating temperatures are limited to 1100°C because of the internal mechanical components (rotating shaft, rabble arms, etc.). Maintenance of internal moving parts would be high because of ship motion as well as thermal stress. Also, the presence of any fusible ash may render the system inoperable.

Multiple chamber incinerators are used extensively for industrial disposal of bulk solid wastes. Liquid wastes can be injected with the auxiliary fuel. Slurries and sludges are not suitable for this type of incinerator because they may fall through the grates. Solids/air mixing is not as thorough as in rotary kilns, and high excess air rates are required which result in maximum operating temperatures of approximately 1000°C.

Emission Controls

Emissions from at-sea incineration are dispersed into the atmosphere without scrubbing. Acidic gases are effectively neutralized by sea water after plume touchdown with no measureable change in sea water pH.

Emission control devices commonly used with land based incinerators for particulate and/or gas scrubbing have many limitations for shipboard applications including size, weight, and water requirements. A high energy venturi scrubber represents the lowest weight, volume, and installed cost emission control system available, if sea water can be used for scrubbing and discharged into the sea. However, marine environmental effects of a single-pass sea water scrubbing system must be evaluated. A closed loop system requiring a settling tank would be impractical because of space and weight requirements.

Waste Feed System

A waste feed system is required to retrieve wastes from storage and transport them to the incinerator without spillage under operating conditions of ship motion. Liquid wastes and some slurries can be transported to the incinerator by conventional pumps, piping, and valves. Solids can be loaded into standard bulk material containers on land. Onboard ship, these containers can be empted directly into the rotary kiln feed hopper. Sealed plastic or fiber containers that can be combusted in the kiln may also be considered. Handling of 55 gallon drums onboard ship is not recommended.

Waste Selection

Wastes can be selected for at-sea incineration only after a complete analysis of their physical, chemical, and thermal properties. Physical properties must be known to determine if the waste is compatible with the type of incinerator and waste handling system. Chemical and thermal properties affect the combustion characteristics of the waste. Normally, a minimum heating value of 3000 to 3600 kcal/kg (5500 to 6500 Btu/lb) is necessary to sustain combustion. The M/T Vulcanus has successfully incinerated organochlorine wastes with chlorine content as high as 63% and heat content as low as 3,860 kcal/kg (6950 Btu/lb) without firing auxiliary fuel. Table 2 lists general types and sources of hazardous wastes available for at-sea incineration.

Onboard Laboratory

It is recommended that space be provided for an onboard laboratory in which relatively simple chemical analysis could be performed. In the case of at-sea incineration of an unusually toxic waste, monitoring to verify adherence to the contamination control aspect of a health and safety plan could be performed by analyzing wipe samples of deck surfaces. Additionally, stack gas samples could be analyzed in the onboard laboratory to determine waste destruction efficiency. During the at-sea incineration of U.S. Air Force stocks of Herbicide Orange, wipe samples of deck surfaces and stack gas samples taken by a benzene impinger train were analyzed onboard the Vulcanus by gas chromatography.

TABLE 2. HAZARDOUS WASTE TYPES AND SOURCES FOR AT-SEA INCINERATION

Waste	Source
Organic Chemical Wastes - Spent solvents - Distillation residues, heavy ends or still bottoms - Off-specification or recalled products	Chemical industry facilities located mainly on the Gulf Coast and Eastern Seaboard
Pesticide and Herbicide Wastes - Filter cake and solids - Wastewater treatment sludge - Distillation residues, heavy ends or still bottoms - Off-specification or recalled products	Manufacturers and suppliers located in nearly all regions of the United States
Petroleum Refining Wastes - Emulsion solids - API separator sludge - Heating exchanger bundle cleaning sludge - Dissolved air flotation (DAF) float - Tank bottoms	Petroleum refineries located mainly on the Gulf Coast, Eastern Seaboard, and West Coast

WATERFRONT SUPPORT FACILITY

A waterfront facility is a critical part of the entire system for disposal of hazardous waste using incinerator ships. A dedicated, full-service facility must accomodate wastes in almost any physical form or type of container, some of which may be old, corroded, or leaking. Ideally, the facility could receive wastes by truck, rail or barge. Capability must be provided for preparing and blending wastes for optimum combustion and for unloading any ash residue from the ship. Figure 1 is a generalized process flow diagram for a facility*.

Facility Requirements

The ideal site would be located where transportation time and distance on land and at sea are minimal. Structural standards must be carefully followed, and these are normally defined by the Uniform Building Code and additional local building regulations. The design must also meet safety, health and environmental criteria, which include provisions for facility monitoring, personnel safety, and contingency planning in the event of both major and minor releases of chemical wastes that have the potential to reach soil, water, or air. A layout of the facility is shown in Figure 2.

Liquid waste, solid waste, and ash residue from incineration will be processed and stored separately. Liquid waste in drums and smaller containers

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* McNeil, D.K., et al., "Design Requirements for a Waterfront Facility to Support Chemical Waste Incinerator Ships", Appendix D to "Report of the Interagency Ad Hoc Work Group.....".

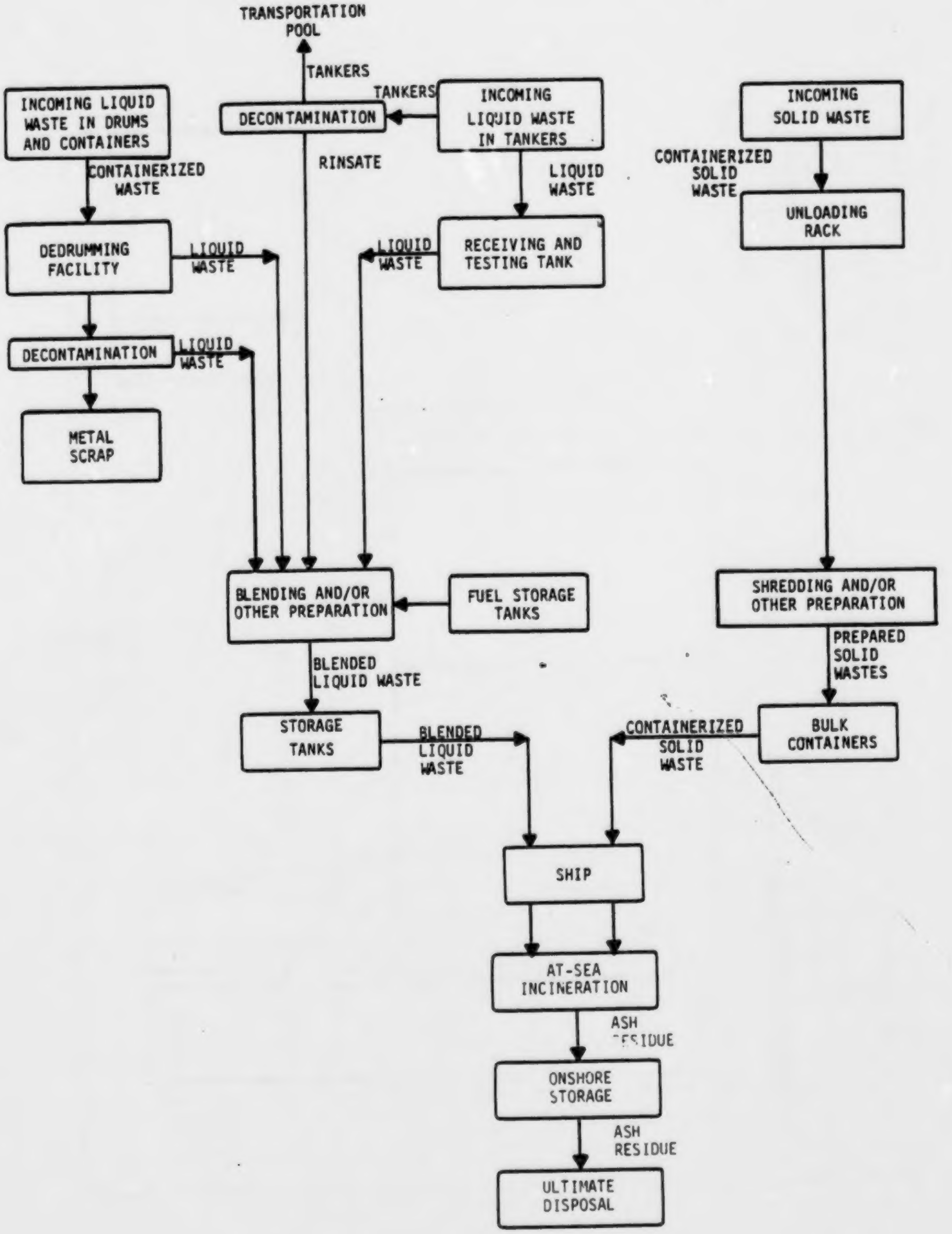
TRANSPORTATION POOL
TANKERS
TANKERS
INCOMING LIQUID WASTE IN DRUMS AND CONTAINERS
DECONTAMINATION
INCOMING LIQUID WASTE IN TANKERS
INCOMING SOLID WASTE
CONTAINERIZED WASTE
RINSATE
LIQUID WASTE
CONTAINERIZED SOLID WASTE
DEDRUMMING FACILITY
LIQUID WASTE
LIQUID WASTE
RECEIVING AND TESTING TANK
UNLOADING RACK
DECONTAMINATION
LIQUID WASTE
METAL SCRAP
BLENDING AND/OR OTHER PREPARATION
FUEL STORAGE TANKS
SHREDDING AND/OR OTHER PREPARATION
BLENDED LIQUID WASTE
PREPARED SOLID WASTES
STORAGE TANKS
BLENDED LIQUID WASTE
CONTAINERIZED SOLID WASTE
BULK CONTAINERS
SHIP
AT-SEA INCINERATION
ASH RESIDUE
ONSHORE STORAGE
ASH RESIDUE
ULTIMATE DISPOSAL

Figure 1. Waterfront Facility Process Flow

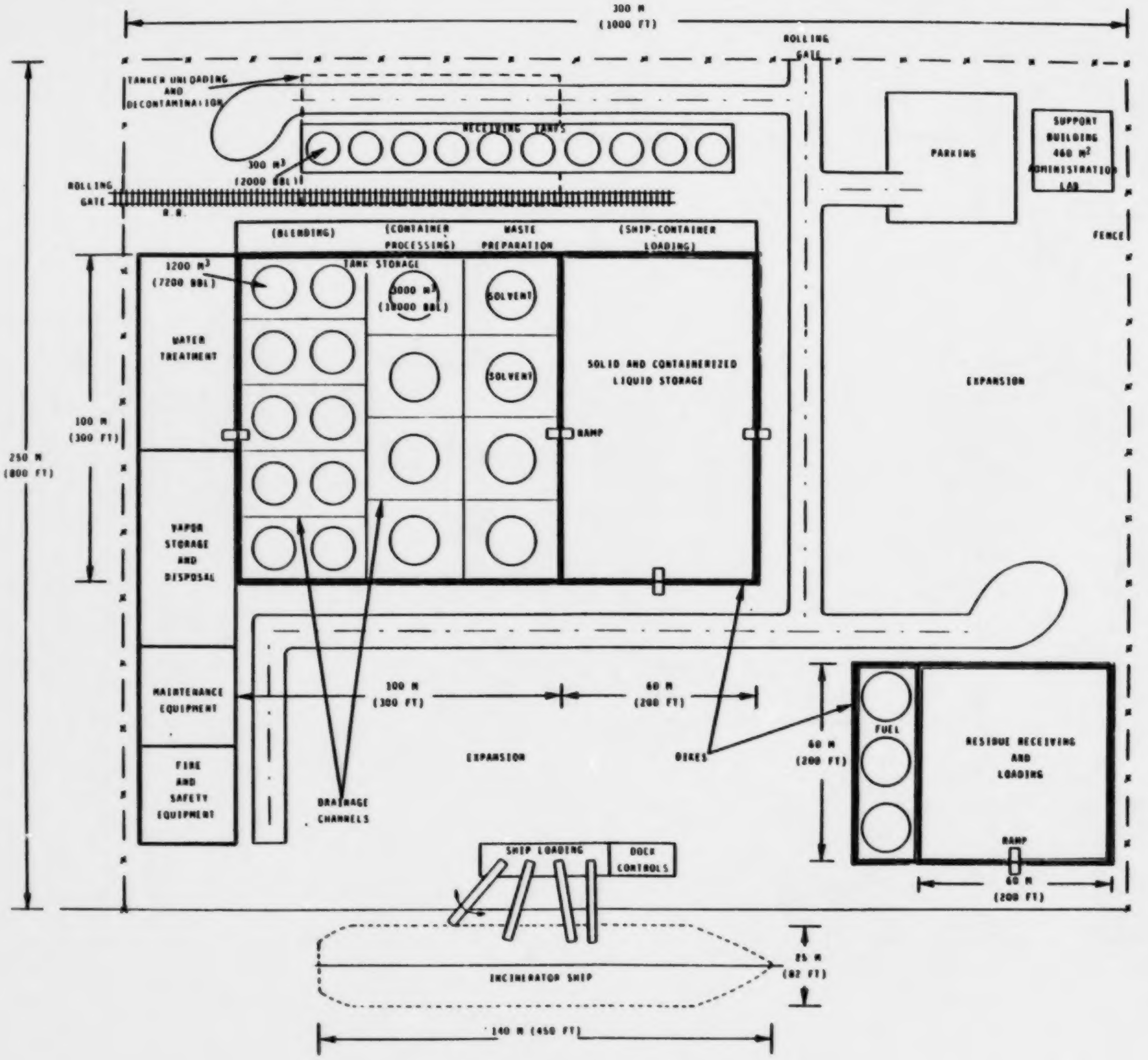
300 M
(1000 FT)
ROLLING GATE
TANKER UNLOADING AND DECONTAMINATION
RECEIVING TANKS
300 M³
(2000 BBL)
SUPPORT BUILDING 460 M²
ADMINISTRATION LAB
PARKING
ROLLING GATE
R.R.
FENCE
(BLENDING)
(CONTAINER PROCESSING)
WASTE PREPARATION
(SHIP-CONTAINER LOADING)
1200 M³
(7200 BBL)
TANK STORAGE
5000 M³
(30000 BBL)
SOLVENT
SOLVENT
SOLID AND CONTAINERIZED LIQUID STORAGE
RAMP
EXPANSION
WATER TREATMENT
100 M
(300 FT)
250 M
(800 FT)
VAPOR STORAGE AND DISPOSAL
MAINTENANCE EQUIPMENT
FIRE AND SAFETY EQUIPMENT
100 M
(300 FT)
60 M
(200 FT)
EXPANSION
DIKES
DRAINAGE CHANNELS
60 M
(200 FT)
FUEL
RESIDUE RECEIVING AND LOADING
RAMP
60 M
(200 FT)
SHIP LOADING
DOCK CONTROLS
25 M
(82 FT)
INCINERATOR SHIP
140 M (450 FT)

Figure 2. Waterfront Facility Layout

will be sent through a shredder in the dedruming facility. Liquid from both the containers and the decontamination of the containers will be blended to optimize handling and combustion processes and pumped to storage tanks. Liquid wastes arriving in tank trucks or tank cars will be blended and pumped to the storage tanks.

Solid waste arriving at the site will be unloaded, prepared for incineration by shredding, and placed in bulk material containers to be loaded on the ship. Any ash residue from at-sea incineration will be returned to the waterfront facility and kept in the residue storage area until removed for ultimate disposal.

Existing Terminal Facilities

A review of existing terminal facilities in the United States was conducted by Diversified Maritime Services, Inc. Facilities that regularly accomodate vessels similar in length and draft to the conceptual incineration vessel were identified, without regard to the type of commodity or material being handled. Only those terminals having minimum water depth at loading berths of 7.6 meters (25 feet) were included. This list of terminals was then reduced to those that are handling either liquid and/or dry cargoes that are hazardous or commodities that possess physical and chemical characteristics that are similar to those anticipated for hazardous wastes (ignitability, corrosivity, reactivity, and toxicity). The latter group of terminals was assessed from the standpoint of their potential for conversion into a marine terminal for handling liquid and/or solid hazardous wastes. Marine terminal and materials handling experts were consulted regarding reasonable and practical alternatives in the development of a hazardous waste marine terminal.

There are 139 ports and 1,221 terminal docks, piers, or wharves on the East, Gulf, and West costs of the Continental U. S. that have sufficient water depth and space to receive the conceptually designed chemical waste at-sea incineration vessel. Of the 1,221 terminal docks, piers, and wharves, 381 handle refined petroleum products or liquefied chemicals (and allied products). These terminals are concentrated primarily in the states of Texas, New Jersey, Louisiana, California and New York. Ownership of terminals other than military terminals is predominantly private as opposed to governmental.

Most of the major and many of the smaller bulk liquid terminal companies that offer terminal services to the public are members of the Independent Liquid Terminal Association (established in 1974). Through that association, they are relatively well informed of environmental rules and regulations that are being developed in compliance with congressional legislation. Accordingly, they are not only familiar with long existing local, state, and federal regulations for handling commercial bulk liquid commodities (which are more concerned with fire, explosion and safety matters), but are also familiar with recent EPA regulations for implementing the Resource Conservation and Recovery Act. Several of these companies have filed or plan to file "Notification of Hazardous Waste Activity," EPA form 8700-12, with EPA Regional Offices in order to qualify their terminals for intermim status. Their knowledge and expertise could contribute to development of a waterfront facility.

CONCEPTUAL VESSEL DESIGN

The conceptual chemical waste incinerator ship has been designed to the highest standards of marine chemical cargo containment and protection, as established by the International Maritime Consultative Organization (IMCO) Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IMCO Resolution A.212(VII)). The IMCO Bulk Chemical Code identifies three classes of chemicals, based on the fire, health, water or air pollution, or chemical reactivity hazards they present. These classifications are the basis for ship cargo protection and survivability standards. The chemical types are:

> Type I, products that require maximum preventive measures to preclude escape of such cargo;
>
> Type II, products that require significant preventive measures to preclude escape of such cargo;
>
> Type III, products that require a moderate degree of containment to increase survival capability in a damaged condition.

The design also incorporates the U.S. commerical maritime standards such as those of the U.S. Public Health Service. Finally, as a commercial vessel, the incinerator ship must satisfy the standards of a classification society, most likely the American Bureau of Shipping, for the purposes of insurance coverage.

The conceptual design is based on a mild steel cargo ship hull. The ship is a combination Type I/Type II hull equipped with extensive auxiliary processing systems to handle and incinerate hazardous chemical waste. The centerline tanks provide Type I protection and the port and starboard tanks provide Type II protection. Most candidate chemicals for incineration at sea are rated Type II chemicals, so this design will be able to accomodate rating changes. Figure 3 shows the general arrangement of the vessel.

Principal characteristics of the conceptual vessel are:

Length overall	129.5 m (425'-0")
Length bet.perp.	121.9 m (400'-0")
Beam, molded	23.8 m (78'-0")
Depth, molded	12.5 m (41'-0")
Draft, full load	7.5 m (24'-7")
Propulsion, max	3320 HP
Service Speed	12 Kts.
Range, naut. miles	5000
Accomodations	40, including 5 scientists and 6 incinerator operators
Lightship	7444 mt, including 1000 mt for incinerators and solid waste storage system
Liquid Waste	7200 mt (7088 lt)
Solid Waste	360 mt (355 lt)
Displacement	16,007 M (15,757 LT)

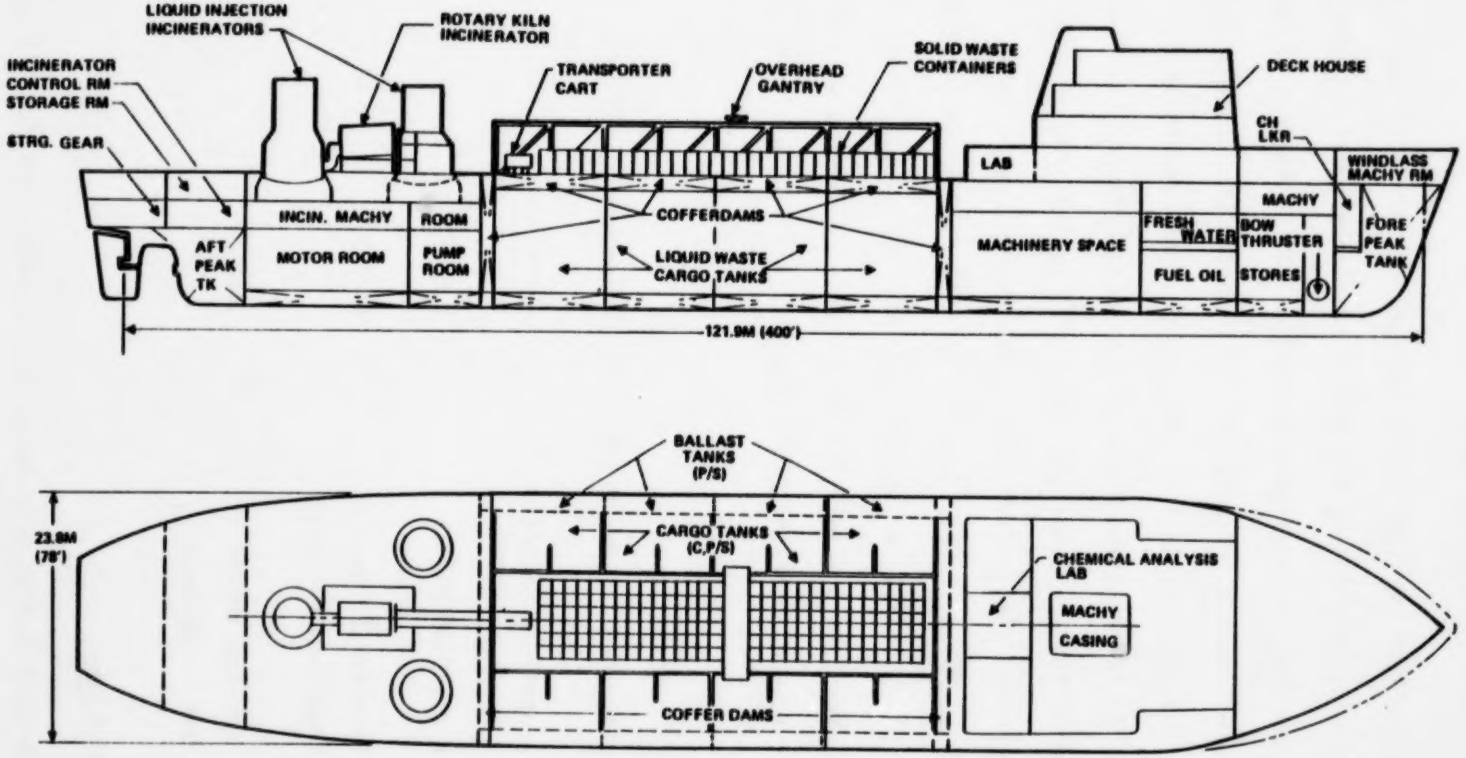
LIQUID INJECTION INCINERATORS
ROTARY KILN INCINERATOR
INCINERATOR CONTROL RM
STORAGE RM
STRG. GEAR
TRANSPORTER CART
OVERHEAD GANTRY
SOLID WASTE CONTAINERS
DECK HOUSE
CH LKR
WINDLASS MACHY RM
LAB
AFT PEAK TK
INCIN. MACHY
MOTOR ROOM
ROOM
PUMP ROOM
COFFERDAMS
LIQUID WASTE CARGO TANKS
MACHINERY SPACE
FRESH WATER
FUEL OIL
MACHY
BOW THRUSTER
STORES
FORE PEAK TANK
121.9M (400')
BALLAST TANKS (P/S)
CARGO TANKS (C,P/S)
23.8M (78')
CHEMICAL ANALYSIS LAB
MACHY
CASING
COFFER DAMS

Figure 3. Incinerator Ship Conceptual Design
IMCO Type I/Type II Combination Hull

Propulsion and Electrical Machinery

The conceptual chemical waste incinerator ship will have a service speed of twelve knots, provided by a diesel electric propulsion plant. Two attributes of the diesel electric machinery determined its selection. First, the diesel generators that supply the power to the electric propulsion motors can be located apart from the motors. In this ship design, the propulsion motors must be located aft, below the incineration system. The diesel generators, however, are installed forward, below the accomodations deckhouse, so that the attended machinery space is separated from the incineration system and the waste cargo. Second, the power produced by the diesel generators can be used for the incineration plant when the propulsion plant is idle or operating at reduced speeds. This "power pool" arrangement makes it possible for the ship to be powered by a single installation, rather than having separate ship's propulsion and ship's service generator installations.

The basic information on the installed machinery follows:

Diesel Generators	5 @ 800 KW
Propulsion Motors	2 @ 1750 HP
Required Propulsion Power, approx.max.	3320 HP
Required Incineration Power, approx.max.	1500 HP

Forward Deckhouse

The forward deckhouse contains the accomodations for all ship's personnel. It is located forward of the cargo areas and incinerator plant so that personnel living and working space are as far away as possible from the incinerator plume, heat and potential chemical contamination. A chemical analysis laboratory is provided on the main deck level with separate entrances to the deck and to the deckhouse, so that chemical samples need not enter the main deckhouse.

Showers and clothing change facilities are provided on the main deck level. This area has lockers so that crew members can leave dirty or contaminated gear at the entryway, rather than having to enter the accomodations areas to disrobe or store dirty gear in their own quarters. The shower facilities also provide emergency first aid washdown for anyone accidentally contaminated by waste chemicals. Medical equipment and hospital facilities are included onboard to provide emergency care for chemical-related injuries and illnesses. Personnel may travel from the deckhouse to the incinerator area via enclosed passageways located port and starboard immediately below the main deck.

Cargo Containment

The cargo is located in the mid-portion of the vessel. Both liquid waste tanks and the solid waste container storage area are in this area. Liquid waste capacity is 7200 cubic meters. The liquid waste tanks all have smooth internal surfaces in order to simplify tank cleaning and minimize the possibility of contamination and corrosion. Cofferdams between the tanks provide separation for incompatible cargoes. Tank specifications include internal epoxy linings, but the selection of tank linings or the development of new tank lining materials for hazardous waste carriage deserves more attention.

Only the four centerline tanks can carry Type I cargoes. The eight port and starboard tanks are for Type II cargoes. They are protect by wide wing ballast tanks greater than the minimum 760 mm(2'-6") required for Type II protection. The large amount of ballast tankage can be sequentially filled to help the shipmaintain a constant draft and uniform ship motions as wastes are incinerated.

The capacity for solid waste is 360 mt. They will be stored on deck within the same boundaries as is the liquid cargo. The solid waste is prepackaged in 2 mt containers, which will be secured within a guide framework that is equipped to transfer the container to the rotary kiln. 180 containers will be stowed on the main deck, single height. The solid waste stowage area and handling equipment directly above the liquid waste cargo tanks are separated from the liquid cargo tanks by a three foot high,inert gas filled void space that extends the full width of the cargo area. Further design will have to receive formal approval from the U.S. Coast Guard.

Incineration Plant

The incinerators and their auxiliaries are located aft. Also located aft are the incinerator machinery room, the incinerator control room, the propulsion motors, and the cargo pumproom. Three vertically mounted, liquid injection incinerators are installed in the stern deck area. One liquid incinerator will be the afterburner for the experimental rotary kiln, to complete the destruction of the waste that may be only vaporized in the kiln. The other two liquid injection units will have no attached kilns. However, any large scale expansion of the solid waste incineration capacity would require that the other two liquid injection units also be used as afterburners for any kilns added later.

The experimental rotary kiln is flanked on both port and starboard by two forward liquid injection incinerators. This location is considered least disruptive to the kiln operations. The kiln/liquid injection incinerator combination is on the centerline, with the two other liquid injection incinerators located outboard of the kiln's forward end. The clearances around all the units should be sufficient for all anticipated deck operations. There is adequate space both on deck and below decks for research and testing areas desired by EPA.

The rotary kiln incinerator drum is mounted with one end higher than the other. Gravity "tumbles" the wastes along the length of the incinerator as it rotates, so that wastes loaded into the upper end are completely burned by the time they tumble to the lower end. The waste residence time in the kiln is determined by rotational velocity and drum angle with the horizontal. The drum axis is parallel to the ship centerline to minimize the effect of roll on the waste residence time. Preliminary estimates of the maximum pitch angle are about 2 1/2 degrees, which is unlikely to disrupt the rotary kiln's operation. Solid waste incineration will be terminated in high seas, and the kiln secured in place.

The ship's vibrations and roll motions impose additional loads on the kiln's external rotary drive. However, two major vibration sources aft, the propulsion motors and the propeller, will be idle much of the time that the solid waste incinerator is operating. They will otherwise be operating at a reduced load. Also, the diesel generators, another major source of induced vibration, are located forward, remote from the incinerators. Therefore, ship source vibrations should not be disruptive to the rotary kiln.

The ash from the kiln will drop into a quench pit at the exit end of the kiln. The ash is estimated to range from one percent to twenty-five percent of the waste, but ten percent is a reasonable allowance. the ash will be retained onboard until the ship returns to its loading terminal, where it can be removed by shoreside equipment. Although it may be possible to discharge solid waste ash overboard if the material is inert, the design has conservatively provided a quench pit large enough to handle residues from the 360 tons of solid waste to be carried.

Solid Waste Storage and Feed System

Solid wastes will be stored on deck in sealed bulk containers, each of 2 mt capacity. One hundred eighty container storage cells will be provided on deck above the liquid cargo tanks. Dockside cranes will place each container into a specified cell of the solid waste storage structure, much as dockside cranes load standard transportation containers into cell guides on cargo ship decks.

Only one container per hour will be delivered to the incinerator, so that only one container at a time needs to be removed from the storage area. A light duty crane, mounted on the overhead structure of the waste container storage area, will remove each container from its cell and deliver it to the transporter on the ship's centerline. The transporter will lock onto both the container and the conveyor and will move the container to the incinerator. At the incinerator, the container will be automatically attached and sealed to the loading hopper of the rotary kiln, the container discharge door will be remotely opened, and the wastes will be gravity fed into the kiln. The transporter will return tne solid waste container to the storage area, where it will be returned to its cell. Stowing the waste containers in specific cells will permit waste incineration to be sequenced, based on the known contents of the waste containers, so that the required operating conditions can be assured. A programmed burn sequence would also make identification of the incinerator contents simpler, in case of incinerator shutdown.

Operating Scenario

The U.S. flag incinerator ship conceptual design is based on the following operating scenario:

- Two week operating cycle, with ten days continuous incineration on site
- Both liquid and solid wastes accepted
- No unidentified "abandoned site" wastes to be accepted
- Solid waste containerized before loading onto ship
- Wastes loaded at terminal by automatic equipment
- Drifting or slow steaming during incineration operations
- Heading into wind maintained by bow thruster during incineration

The ship will have two days to load 7200 mt of liquid waste and 360 mt of containerized solid waste, as well as fuel oil and ship's stores. The vessel will then proceed at 12 knots to a designated waste incineration site, about 100 miles offshore and perhaps 175 miles from the loading terminal. The incinerators will be preheated during the last six to ten hours of this passage so that chemical burning can begin upon arrival at the burn site. Incineration will continue for ten days, during which time the vessel will drift and maintain a heading into the wind (about 60 to 90 degrees), so that the plume from the incinerators is carried away from the ship, rather than falling onto the ship's deck. A bow thruster will be used to maintain the optimum heading to the wind. After completing the incineration, the vessel will return to the loading terminal.

Construction and Operating Costs

Estimated construction and operating costs for the concept design incineration vessel are:

JULY 1980 BASE PRICES (millions of $)

Contract Drawings	$ 1
Construction Contract (1)	$50
Spares, Plan Approval and Inspection	$ 1
TOTAL =	$52
	===
ESTIMATED FINAL COSTS (2) =	$75
Schedule	30 months
Operating Cost(3)	$1,096,000 per voyage ($145 per metric ton of waste)

NOTE (1) Includes $14 million for the subcontracted incineration systems.

(2) Estimated final prices are based on a contract award date of October 1982 and a delivery date of March 1985. 10% per annum inflation rate is assumed.

(3) Estimated cost for start of operation in 1985. Includes ship capital cost depreciated over 15 years and all ship related operating costs, but does not include special risk insurance, waterfront support facility, and waste land transportation costs.

SUMMARY

Thermal destruction of chemical wastes at sea by European vessels has been shown to be an environmentally acceptable and cost effective means of disposal for many types of combustible liquid chemical wastes. EPA has recommended that a U. S. incinerator ship be built to perform operational destruction of liquid wastes and to extend the capabilities of at-sea incineration to destruction of solid and semi-solid materials.

Based upon evaluation of potentially applicable alternatives, the selected incineration system for destruction of both solid and liquid hazardous wastes at sea is a rotary kiln coupled to a liquid injection incinerator. Liquid injection incinerators, proven effective in at-sea operation, should be utilized for destruction of liquid wastes. A single rotary kiln should be installed in combination with one of the liquid injection incinerators for R&D evaluation before additional kilns are added.

A waterfront facility is essential to support the operation of incinerator ships. The facility must be designed to receive, store, analyze, process, and load wastes aboard ship in a safe and efficient manner, and to receive any residues from the incineration process for ultimate disposal. There are numerous existing private and military terminals that may be used for this purpose.

A conceptual chemical waste incinerator ship has been designed to accomodate three liquid injection incinerators and one experimental solid waste rotary kiln incinerator, plus the auxiliary equipment and the waste handling systems needed to support the incineration plant. The new vessel should be able to destroy a total

of 7200 mt of liquid waste and 360 mt of containerized solid waste during ten days of continuous incineration. Estimated cost of the vessel is $75 million, including installed incineration equipment, for delivery in 1985. Operating cost is estimated at $1,096,000 per voyage, or approximately $145 per metric ton of waste.

A U.S. incinerator ship can serve two broad functions: first, it can be used for the destruction of hazardous wastes in a location minimizing the risk to public health and the environment; second, it would provide a safe site to continue EPA's research and development efforts in hazardous waste incineration. An incineration vessel would expand the experience in the large scale incineration of hazardous waste materials. The effects of process variations in commercial scale incinerators on hazardous waste destruction efficiencies need to be further investigated, including many types of wastes not yet tested. In addition to performing operational destruction of hazardous wastes, the proposed incineration vessel could be effectively utilized for verification testing of incinerator designs, emission control concepts, and improved sampling/monitoring equipment and methodology.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the technical direction and cooperation afforded by the members of the Interagency Ad Hoc Work Group for the Chemical Waste Incinerator Ship Program, particularly the Co-Chairmen, Mr. Russell H. Wyer, U.S. Environmental Protection Agency, and Mr. Daniel W. Leubecker, U.S. Department of Commerce, Maritime Administration.

OCEAN INCINERATION/ONSHORE PROCESSING

D. L. HENRY
At-Sea, Inc.
Greenwich, CT

ABSTRACT

At the present time, specific regulations and/or design/performance criteria do not exist for a marine terminal/tank farm complex to support ocean incineration operations. Therefore, the design process requires continuous interfacing and subjective interpretation of regulations and interim guidelines emanating from local, state and federal agencies that may or may not be involved in permitting. The paper will address the "interfacing process" and the presently understood operational requirements of such a facility.

COMBUSTION REACTION CONTROL

G. C. TERRELL
Conservation Technologies, Inc.
Bristol, RI

ABSTRACT

A new modification of suspension firing techniques is reported. The key feature of this technique is the establishment of a stable but physically extended reaction zone. Separate and independent control of the feed rates of the reactants (feedstock and air) enable a wide range of oxygen excess or deficiency conditions to be maintained. Controllable heat energy feedback also enables independent control of equilibrium temperature at an arbitrary point of excess oxygen or of oxygen starvation.

The achievement of controllable steady state conditions at different sets of values of the independent variables makes it possible to derive better knowledge of the process dynamics by sampling and analysis of the process products. There are two important outcomes of this capability. The first is that it becomes possible to utilize real time computer control to operate the system. The second is that it becomes possible to utilize computer aided design procedures to calculate and design large scale systems.

This paper reports on the details of the application of this concept to the design of a system for handling a particular type of hazardous waste; namely, tanning industry wastes containing significant quantities of chrome salts which it is desired to control, recover, and recycle.

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I. Introduction

Rising costs of fossil fuels are inspiring more and more industrial generators to consider the potential fuel value of various waste products from manufacturing. One of the more difficult classes of waste materials from which energy values may be extracted is wastewater treatment sludge. The problem is the relatively heavy water content which functions as a heat sink. As a consequence, sludges have been notorious as heavy consumers of auxiliary fuel. The development work done by Conservation Technologies, Inc. has been directed specifically to the attainment of the highest possible efficiency of combustion of this class of materials. The result has been to achieve a high rate process with a novel configuration. Observation of the dynamic behavior of the resulting system indicates a capability for flexibility of and close control of reaction conditions.

II. Physical Considerations - Theory of Operation

Because a combustion reaction is in fact a chemical reaction involving atoms, the first principle invoked is that of giving the atoms involved the best possible chance of being involved in an encounter in the shortest possible time. In the method being reported today, this is accomplished by utilizing a commercial device known as a jet mill as a combustion chamber. The combustion air at the proper temperature is fed to the chamber at the proper rate to establish a high velocity recirculating gas stream in the chamber. The feedstock, or sludge, is injected separately in finely divided form by spraying. All of the process consequences flow directly from these mechanics.

A. Recirculation Ratio

Reference is made in the first paragraph to a high velocity recirculating gas stream. This is a characteristic of jet mill functioning which is not immediately obvious to everyone. Look at the arrangement shown in Figure 1. Air is pumped at a constant rate by way of the Duct A to the nozzles B and subsequently exits by way of the Duct C which has the same cross-sectional area as Duct A. If one measures with a pitot tube the velocity pressure in Duct A and in Duct C, one will determine that the same amount of air is leaving the system as is entering. If, however, velocity pressures are measured in the jet mill at, for instance, point D, one will discover that there is apparently several times as much air flowing past point D. Figure 2 is a graph which shows the measured recirculation ratio versus the mass flow rate of air in Ducts A and C for a particular device. Physically, recirculation is a result of the fact that momentum is initially imparted to the air by the process of injecting it through nozzles in the direction in which it is desired to establish the flow and the fact that the exit branch is installed with its axis normal to the fluid flow lines in the mill.

The operational significance of this recirculation phenomenon is that it makes it possible to establish in the mill velocities of such magnitude that relatively large particles can be entrained while at the same time moderate velocities are maintained in Ducts A and C.

B. Mean Gas Particle Residence Time

Strictly speaking, the recirculation phenomenon is a statistical process. Visualize the air being pumped into the system as composed of a large number of discrete particles so that we can identify a particular particle as it enters and leaves the system. A recirculation ratio of 3.5 to 1 does not mean that each particle of air which enters

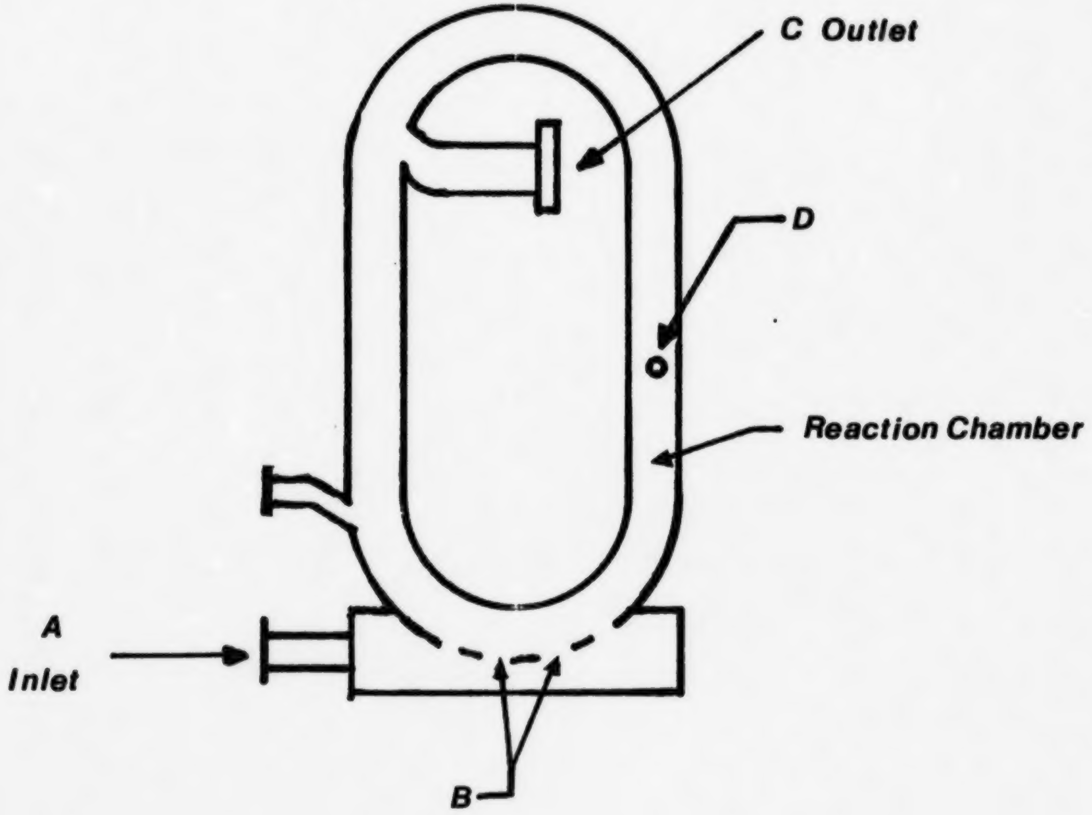

C Outlet
D
Reaction Chamber
A
Inlet
B

Fig. 1

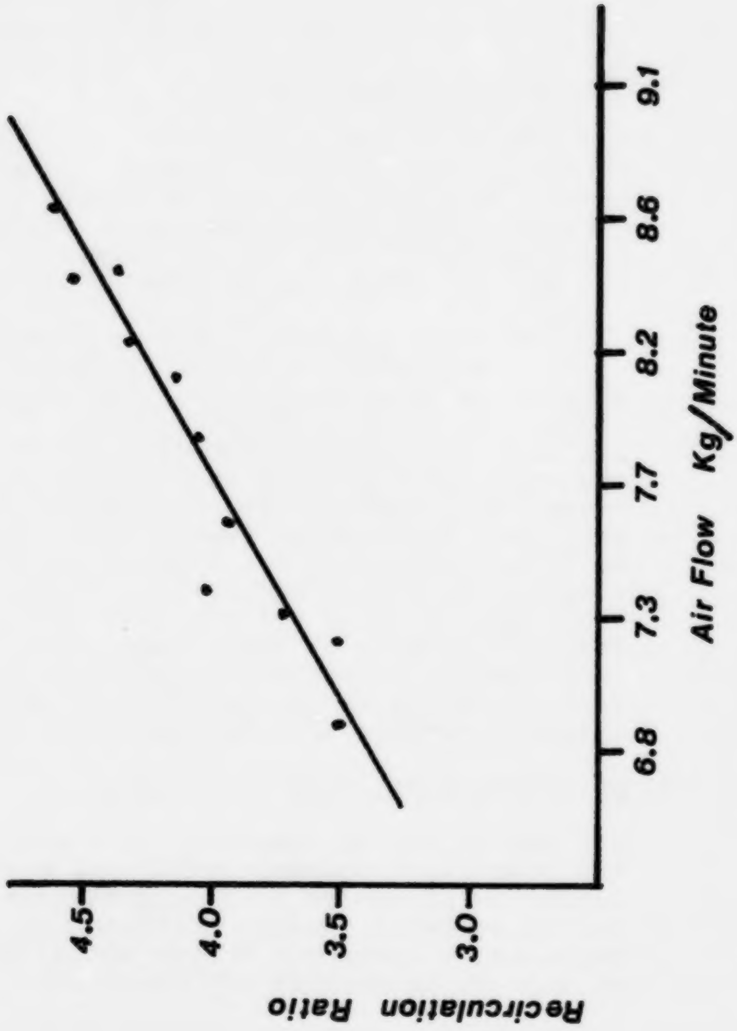

Recirculation Ratio
4.5
4.0
3.5
3.0
6.8
7.3
7.7
8.2
8.6
9.1
Air Flow Kg/Minute

Fig.2

makes 3.5 circuits of the mill before it appears at the exit. Observe in Figure 1 the four changes in direction of flow in the course of one circuit of the chamber. This causes turbulence and turbulence means good mixing. Which particular particles of air may be appearing in the exit duct at any given moment is a random event. A recirculation ratio of 3.5 means that the mean number of circuits made by all of the particles of air is 3.5. Some will make much less and some will make much more. The mean residence time of the air in the mill can be calculated as:

$$\bar{T} = rL/v \text{ - - - - - - - - - - - - - - - - - -(1)}$$

where $\bar{T}$ = mean residence time (seconds)
r = recirculation ratio
L = centerline length of toroidal circuit (feet)(meters)
v = actual velocity in chamber (feet/sec.)(meters/sec.)

C. Particle Size Distribution

Reference was made to the injection of the feedstock or sludge in the form of a spray. Figure 3 shows the arrangement of Figure 1 with the injection of the sludge shown schematically. The sludge as it emerges from the nozzle is blasted into a spray in the direction of flow of the air in the mill by small jet of high pressure air.

The characteristics of this type of nozzle are well known. Measurements on the spraying of sludge were reported in 1971 by Ishii et. al.(1). The subject sludge had a water content of 79% and an ash content of 13.2%. Samples for particle size measurement were collected by capturing from the spray with glass plates coated with vacuum pump oil. Figure 4 illustrates typical particle size distributions. Note that for a given size nozzle, there is a decided shift to finer particle sizes with increased flow rate at the nozzle. Note that the particle sizes generally range from vanishing to about 800 microns. Sauter's mean diameter ranges from 660 microns at lower feed rates to 465 microns at higher feed rates. Sauter's mean diameter is the diameter of that particle which has a specific surface area equal to the mean specific surface area for the whole group.

D. Entrainment and Drag Coefficient

The object of creating the conditions such that the gas in the combustion chamber (mill) has a high velocity and the sludge is presented in finely divided form is so that all of the solid matter become entrained by the gas. Since we are going to be pumping a steady stream of matter into the chamber, we want to be sure it all comes out.

To keep a particle entrained in a moving stream of gas implies that there are forces acting on it. If the flow were

(1) Ishii et. al., High Performance Incineration of Sewage Sludge, Proceedings of Fourth Annual Northeastern Region Antipollution Conference, July 1971.

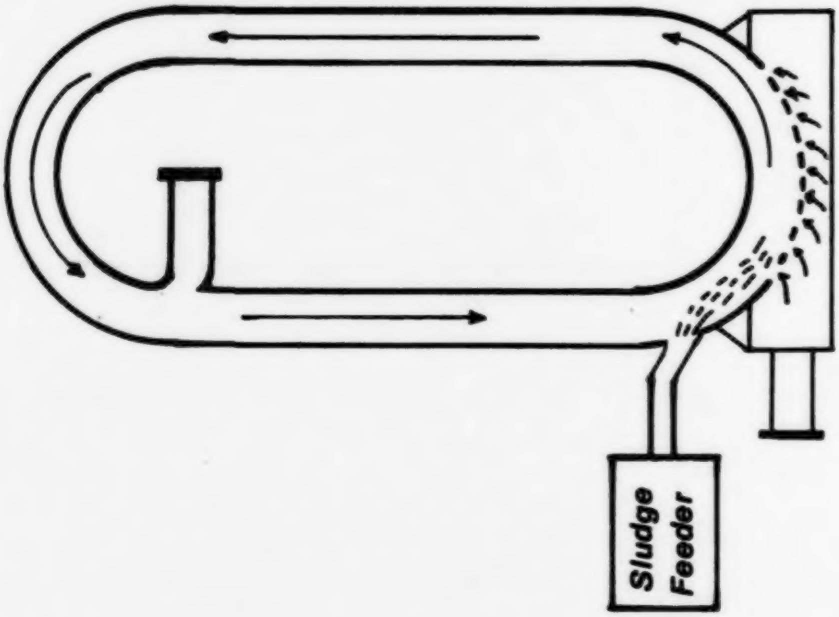

Sludge Feeder

Fig.3

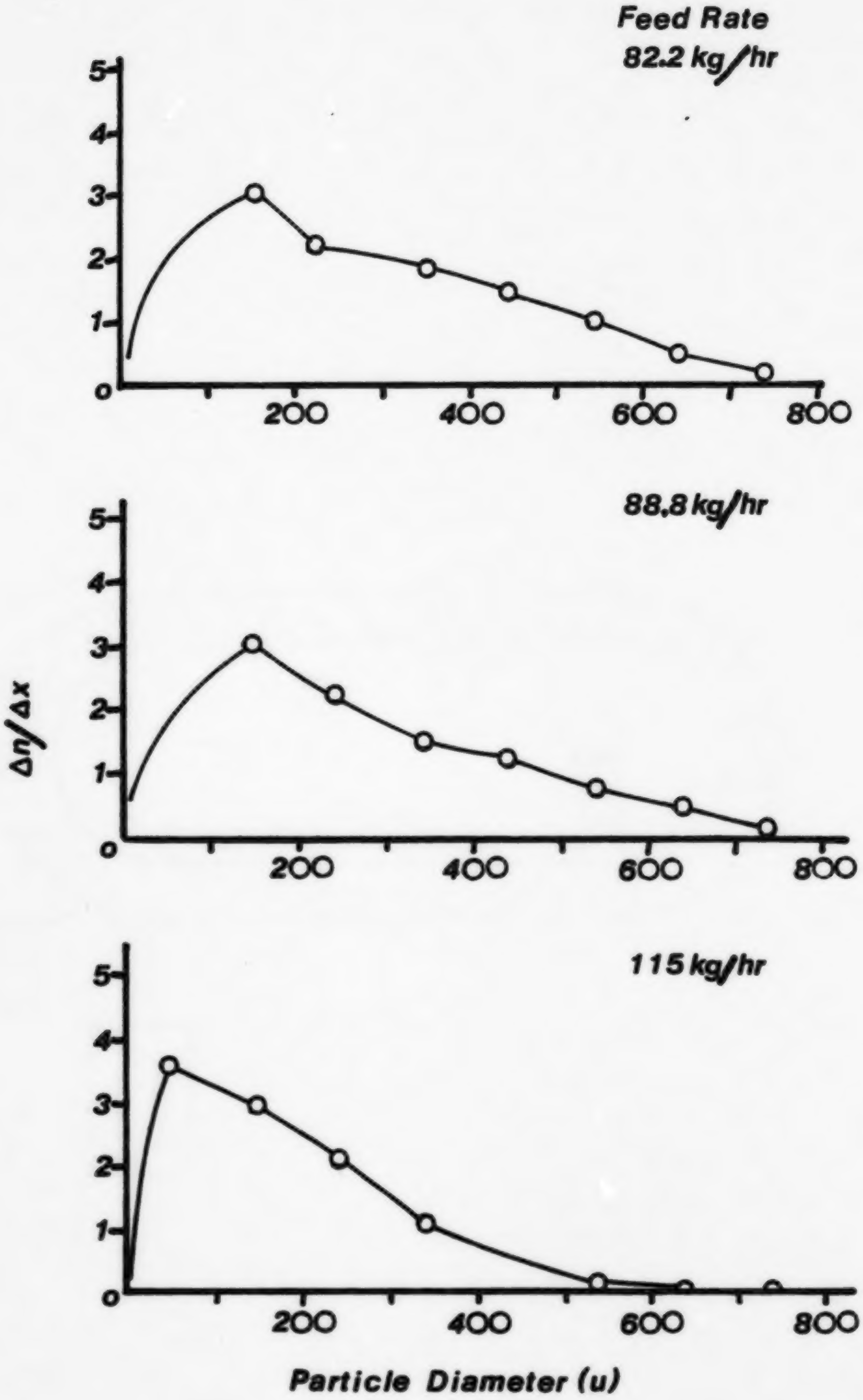

Feed Rate
82.2 kg/hr
88.8 kg/hr
115 kg/hr
Δn/Δx
0
1
2
3
4
5
200
400
600
800
Particle Diameter (u)

Fig. 4

suddenly stopped, everything would be pulled to the bottom by the force of gravity.

The force which keeps a particle entrained is the force which results from the action of the gases flowing over the surface of the particle. In other words, the particle cannot be entrained unless there is relative motion between the particle and the gas. The particle has to "slip" relative to the gas. Therefore, each particle will be traveling at a velocity which is less than the gas velocity by some amount. This amount will be related to the size of the particle. Figure 5 is a curve showing terminal velocities of water droplets in standard air as a function of the size of the particle. Terminal velocity is the velocity at which the drag force (acting upward) just balances the force of gravity (acting downward). Operationally, the reactor described in this paper maintains gas velocities in the order of 9000 feet per minute (2743 meters/min.) or 150 feet per second (45.7 meters/sec.). As Figure 5 shows terminal velocities range from about 3 feet per second (.914 meters/sec.) for 200 micron particles to 16 feet persecond (to 4.88 meters/sec.) for 1300 micron particles. Entrained particles, then would have velocities of from 14 feet per second (44.80 meters/sec.) to 134 feet per second (40.84 meters/sec.) depending upon the size of the particle, (assuming that terminal velocities in the hot combustion atmosphere would not vary materially from those that are found in standard air). In a reactor, the circuit length of which is 24 feet (7.3 meters) the time required for a particle to make one circuit at these velocities ranges from 0.16 seconds to 0.18 seconds, depending upon the size of the particle. Assuming that the recirculation behavior of small solid particles is approximately that of a hypothetical air particle, i.e., a mean recirculation ratio of about 3.5 single circuit transit times of 0.16 to 0.18 seconds translates into estimated residence times of 0.56 to 0.63 seconds.

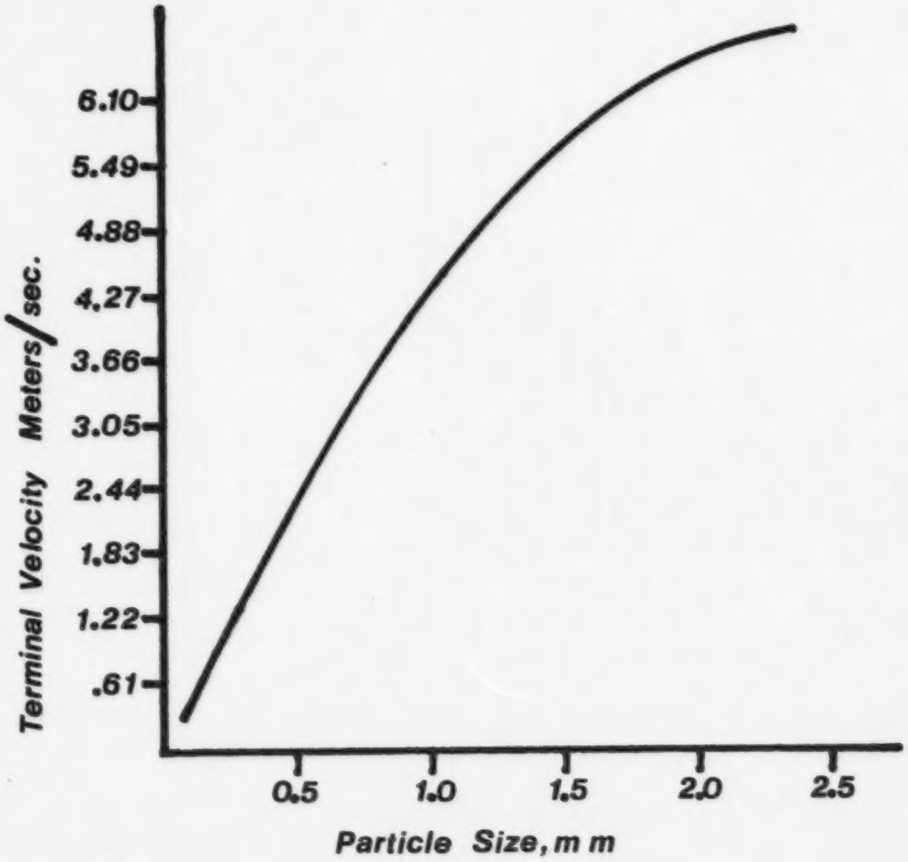

Terminal Velocity Meters/sec.
6.10
5.49
4.88
4.27
3.66
3.05
2.44
1.83
1.22
.61
0.5
1.0
1.5
2.0
2.5
Particle Size, m m

Fig.5

III. Experimental Conditions

A. Process Flow Diagram

Figure 6 shows a flow diagram of the experimental system. Combustion air A_1 is pumped by the pump U to the reaction chamber N at the desired mass flow rate. Simultaneously, sludge F_3 is pumped by the feeder M at the corresponding desired solids rate. The air, on the way to the reaction chamber, passes through heat exchanger Q where it picks up heat energy from the exhaust products of combustion and through the auxiliary burner T where it picks up whatever added energy it needs by firing fuel F_1 with its combustion air A2 . After reacting, the products of combustion pass through the cyclone separator section O where the preponderance of the solids are removed. The relatively clean gases then go to afterburner section P where whatever desired temperature increase is achieved by firing fuel F_2 with air A_3 . The products of combustion are then passed through the heat exchanger Q for exchange with the incoming air. Any remaining heat above a temperature of 300°F(149°C) is removed by generating hot water with heat recovery unit R. Final emissions are controlled with fabric filter S.

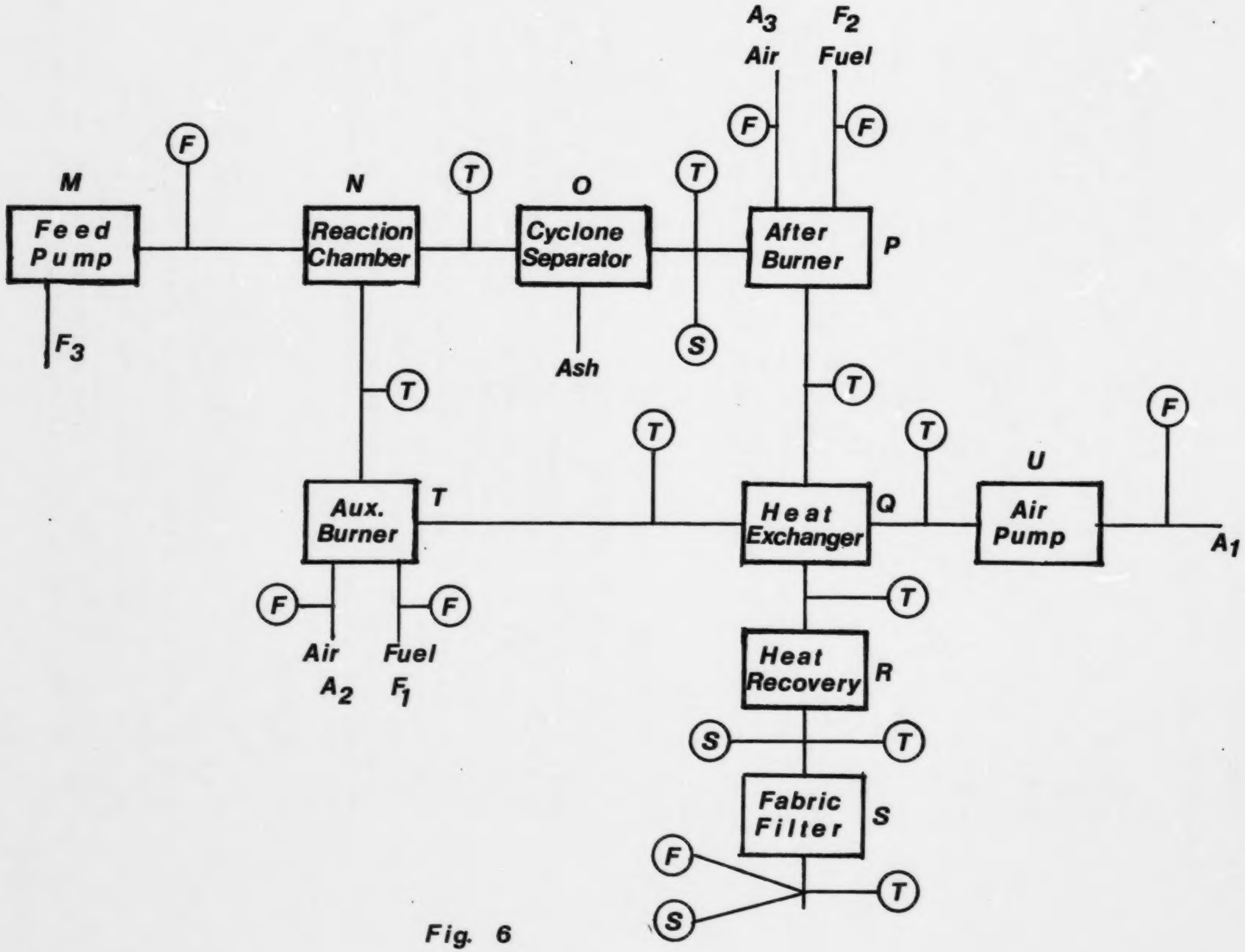
B. Parameters

1. Continuous

Temperature measurement points are indicated on the flow diagram of Figure 6 by the symbol T. These measurements are made by type K thermocouples, the output of which is connected to a Fluke Datalogger which can be programmed to give a print-out of all inputs at any desired time interval. Flow rate of products of combustion, downstream of the fabric filter, is measured by a Hoffer turbine flowmeter, the output of which is also connected to the Datalogger. Mass flow rate of combustion air A_1 is measured by a calibrated ammeter on the pump motor, another automically recorded signal. The ammeter readings were calibrated against the turbine flowmeter by running low temperature air through the system.

2. Discrete

The flows of air A_2 and A_3 , as well as fuel F_1 and F_2 are measured with Dwyer rotameters. These meters are read and recorded periodically throughout a run or whenever a deliberate change is made in their feed rates. The feed pump M which supplies the sludge F_3 is driven by an SCR controlled DC motor. For any specific feed material, before running a test, the feed system is removed from the reaction chamber and timed weight tests are run to develop a calibration curve on the SCR controller.



A3
Air
F2
Fuel
F
F
M
Feed Pump
F3
F
N
Reaction Chamber
T
O
Cyclone Separator
Ash
T
S
After Burner
P
T
T
Aux. Burner
T
F
F
Air
A2
Fuel
F1
T
T
Heat Exchanger
Q
U
Air Pump
F
A1
T
Heat Recovery
R
S
T
Fabric Filter
S
F
S
T

Fig. 6

Points labeled S on Figure 6 are gas sampling ports. At discrete intervals these points are sampled for particulate loading, analysis of particulate, and analysis of the gases.

C. Estimation of Extraneous Losses

To measure extraneous losses, the system is set to run with heated air only. Pump U is set to run at a constant rate, fuel F_1 and Air_2 are set at that constant rate needed to maintain the desired temperature into the reaction chamber. When equilibrium is achieved (a relatively stationary set of temperature readings across the system) the complete set of temperatures and the mass flow rate according to the Hoffer turbine meter at the system output is measured. With these numbers, the temperature decrease from point to point along the system enables the energy loss rate for each system element to be calculated. This type of measurement, of course, can be made for a range of input temperature levels and mass flow rates. Figure 7 is a family of curves measured on the pilot plant.

IV. Measurements

A. Analysis of Test Materials

For the purposes of this investigation, three different but similar wastewater treatment sludges were used. Table 1 lists the basic characteristics of these materials.

B. Description of Running Data

Runs were made using a different level of excess air for each material. All materials were run at three different combustion chamber temperatures, 1200°F (649°C), 1100°F (593°C), and 1000°F (538°C) by adjusting a by-pass valve so as to regulate the amount of energy fed back to the combustion chamber via the combustion air supply. Sludge feed rate was determined by running a calibration curve for each material, using the numerical graduations on the SCR controller to run timed weight tests. Air and products of combustion flow rates were measured by or referenced to the turbine flow meter. Samples of ash were taken for each run and loss of weight on ignition determined by placing in an oven at 550°C (1022°F) for one hour. The basic running data is given in Table 2.

C. Energy Balances

Energy balance calculations are summarized in Tables 3, 4, 5, and 6. In each case, the theoretical energy available is calculated from the test data on each material. Comparison calculations were done using Wilson's formula (Wilson; Prediction of Heat of Combustion of Solid Wastes from Ultimate Analysis, Environmental Science and Technology, Volume 6, Number 13, December, 1972) but the formula grossly

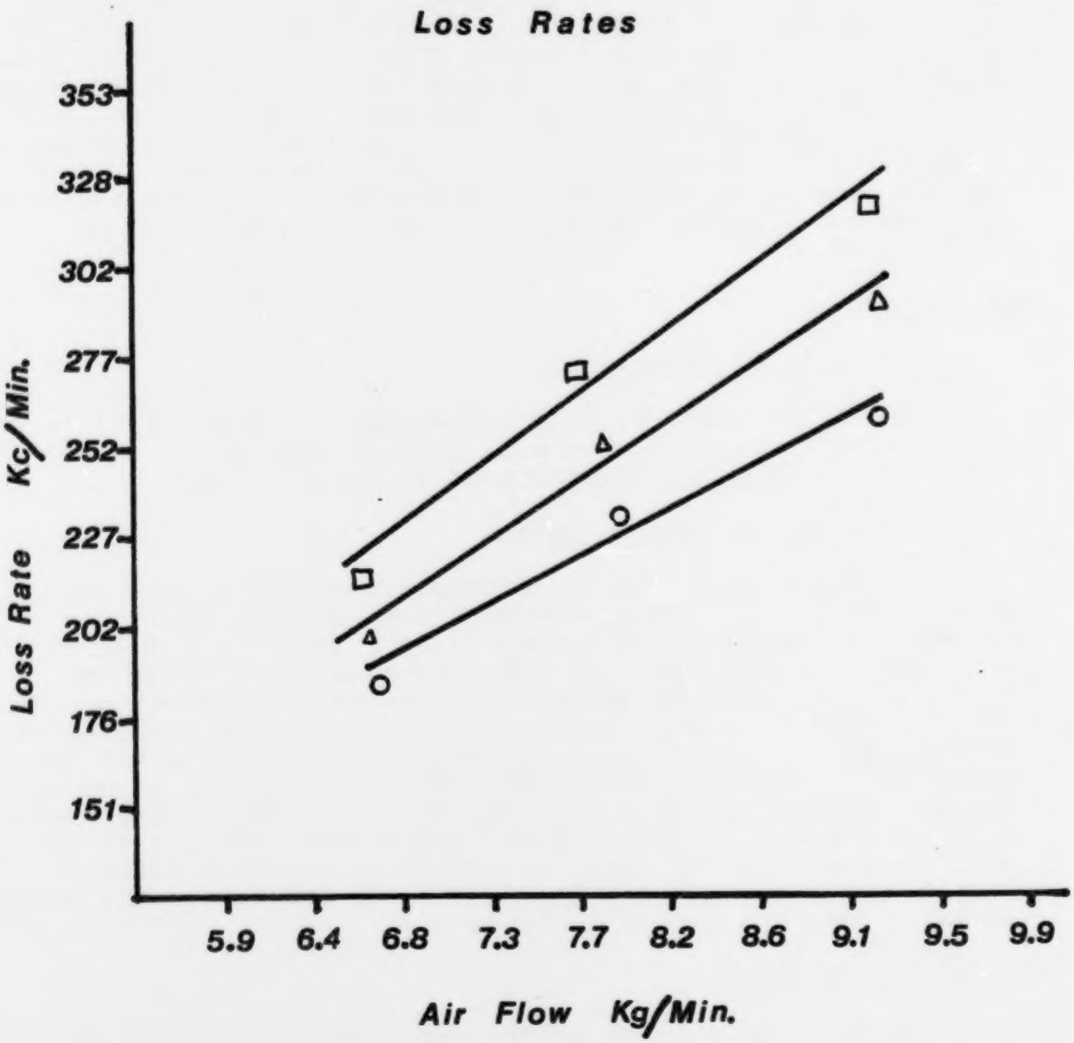

Loss Rates
353
328
302
277
252
227
202
176
151
Loss Rate Kc/Min.
5.9
6.4
6.8
7.3
7.7
8.2
8.6
9.1
9.5
9.9
Air Flow Kg/Min.

Fig.7

TABLE 1 ANALYSIS OF TEST MATERIALS

	Test No. 1	Test No. 2	Test No. 3
Moisture Content	73.5%	68.7%	72%
Dry Solids Fraction	.265	.313	.280
Volatiles, Fraction of Dry Solids	.578	.575	. 65
Ash, Fraction of Dry Solids	.422	.425	. 35
Ultimate Analysis, Fraction of Dry Solids			
Carbon	.3837	.3744	.3151
Hydrogen	.0577	.0568	.0503
Oxygen	.0826	.0582	.2237
Nitrogen	.0457	.0799	.056
Sulfur	.0083	.0057	.005
BTU/LB., Calorimeter Bomb	7891	7274	6463
Kc/Kg	902	831	739

TABLE 2 RUNNING DATA

	Test No. 1	Test No. 2	Test No. 3
Lbs./Min., Sludge Feed(Kg/min)	6.04(2.74)	6.71(3.04)	6.43(2.92)
Lbs./Min., Combustion Air(Kg/min)	11.58(5.25)	16.91(7.67)	12.9 (5.85)
Percent of Stoichiometric	120	134	163
Lbs./Min., Total P.O.C.(Kg/min)	16.88(7.66)	22.35(10.14)	18.6(8.44)
Auxiliary Fuel, Firing Rate, CFH	0	0	0
Feedback Temp., 1200°F(649°C)	226°F(107.7°C)	200°F(93.3°C)	700°F(371°C)
Feedback Temp., 1100°F(593°C)	114°F(45.6°C)	152°F(66.7°C)	837°F(447.2°C)
Feedback Temp., 1000°F(538°C)	120°F(48.9°C)	125°F(51.7°C)	675°F(357.2°C)
Volatiles, % of Ash, 1200°F(649°C)	3.6	4.7	6.7
Volatiles, % of Ash, 1100°F(593°C)	5.9	7.3	8.6
Volatiles, % of Ash, 1000°F(538°C)	11.4	10.9	13.3

TABLE 3 CALCULATED ENERGY AVAILABLE, BTU/MIN.

	Test No. 1	Test No. 2	Test No. 3
Lbs./Min., Sludge Feed Rate(Kg/min)	6.04(2.74)	6.71(3.04)	6.43(2.92)
Lbs./Min. Dry Solids Feed Rate(Kg/min)	1.6 (.726)	2.1 (.953)	1.8 (.816)
Heat Energy Avail., BTU/Lb. Kc/Kg	7891(902)	7274(831)	6463(739)
Total Available, BTU/Min. Kc/min.	12,625.6(3182)	15,275.4(3849)	11,633.4(2932)

TABLE 4 CALCULATED ENERGY LOST AND ABSORBED, BTU/MIN. (KC/Min.

	Test No. 1	Test No. 2	Test No. 3
Combustion Chamber Temperature			
(649°C) 1200°F	12,831.4(3234)	15,215.1(3834)	13,559.4(3417)
(593°C) 1100°F	12,166.3(3066)	14,384.4(3625)	12,899.9(3251)
(538°C) 1000°F	11,511.2(2901)	13,583.9(3423)	12,220.5(3080)

TABLE 5 CALCULATED ENERGY SUPPLIED BY FEEDBACK, BTU/MIN. (KC/MIN.)

Combustion Chamber Temperature	Test No. 1	Test No. 2	Test No. 3
(649°C) 1200°F	351(88.5)	408(103)	1860(466)
(593°C) 1100°F	38(9.6)	209(52.7)	2280(575)
(538°C) 1000°F	55(13.9)	102(25.7)	1781(449)

TABLE 6 NET ENERGY TO BE SUPPLIED BY SLUDGE, BTU/Min. (KC/MIN.)

Combustion Chamber Temperature	Test No. 1	Test No. 2	Test No. 3
(649°C) 1200°F	12,480.4(3145)	14,807.1(3731)	11,600.(2923)
(593°C) 1100°F	12,128.3(3056)	14,175.4(3572)	10,619.9(2676)
(538°C) 1000°F	11,456.2(2887)	13,481.9(3397)	10,439.5(2631)

overestimates the heat available relative to the calorimeter bomb tests except for the third material. Therefore, the test values were used in all cases. Energy leaving the combustion chamber via of the products of combustion was estimated using the change of enthalpy for the components. Losses were estimated from the curve of Figure 7. Since no auxiliary fuel was needed for any of these materials, energy entering the combustion chamber was estimated by calculating the change in enthalpy of the combustion air for each of the temperatures recorded. The difference between the energy leaving and entering was assumed to be the energy contributed by the combustion of the sludge. These are the values listed in Table 6.

D. Burn-out Fraction

If the values listed in Table 6 are each divided by the appropriate value of theoretical heat of combustion available, a fraction is obtained which we have called the fraction of total burn-out achieved. These values should correlate roughly with the energies associated with the residual volatiles found in the ash samples. Note that, approximately, the energy supplied by feedback which is listed in Table 5, should equate to the energy which the sludge fails to supply, which is associated with the volatiles found in the ash. Visually, this is substantially all fixed carbon. If we assume this is the case and calculate the energies associated with this weight loss of the ash, we get the values listed in Table 8. If we compare the values in Table 8 with the values in Table 5, we find a reasonable degree of agreement except for test Number 3. Since there is more energy missing than can be accounted for in the ash, we must assume that there are incompletely oxidized components in the gaseous products of combustion. A further investigation into this aspect is indicated.

E. Summary and Conclusions

Work with this system has indicated that we have a concept which is amenable to reasonably close control and adjustment. Independent positive control of both solids and combustion air feed rates in a sealed system allows for arbitrary selection of reaction conditions. The chosen reaction conditions remain reasonably stable unless an input rate is deliberately changed. Response of the reaction conditions to step changes of inputs is reasonably rapid and the new equilibrium is stable. It appears that this is a useful system for experimental work in which control of reaction conditions is important to the task of resolving cause and effect relationships.

TABLE 7 FRACTION OF TOTAL BURNOUT ACHIEVED

	Test No. 1	Test No. 2	Test No. 3	Avg. Over Excess Air
Percent Excess Air	20	34	63	
Combustion Chamber Temperature				
(649°C) 1200°F	.988	.969	1.006	.988
(593°C) 1100°F	.961	.928	.913	.934
(538°C) 1000°F	.907	.882	.897	.895
Avg. Over Temperature	.952	.926	.939	

TABLE 8 ENERGY REPRESENTED BY VOLATILES IN ASH BTU/MIN. (KC/MIN)

Combustion Chamber Temperature	Test No. 1	Test No. 2	Test No. 3
(649°C) 1200°F	90.3(22.8)	183.8(46.3)	140.7(35.5)
(593°C) 1100°F	147.6(37.2)	285.5(71.9)	212.4(53.5)
(538°C) 1000°F	285.6(72)	426.3(107)	328.5(82.8)

DESIGN AND OPERATION OF A VERSATILE POLLUTION CONTROL/LIQUID WASTE THERMAL DESTRUCTION SYSTEM WITH MAXIMUM ENERGY RECOVERY

F. HASSELRIIS, R. MONRO and D. KONNICK
Combustion Equipment Assoc., Inc.
New York, NY

ABSTRACT

The paper describes the design and operation of a versatile facility for destruction of phenolic fumes in a thermal oxidizer with fume preheat and a waste heat recovery, designed, built and operated by CEA, selling steam and up to 500 KW of power to a phenolic laminate manufacturer.

During the four years of operation, this facility has gradually substituted selected liquid wastes for No. 6 oil as fuel, and now consumes several million gallons per year.

The design and operation of the plant to accept nearly constant fume flow while delivering reliable steam at highly variable flow rates was achieved by providing over 2:1 range of firing and a steam accumulator to absorb laminating press peak loads. Thermal efficiency is 88 percent to 95 percent.

The pre-combustor burner, 400F fume preheat and 1500-2200F furnace temperature assure oxidation of all liquid wastes accepted under a manifest system from waste collectors and industrial clients.

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INTRODUCTION

The desire for a clean environment and the passage of more stringent emission regulations in the 1970's forced many manufacturers of industrial laminates to install thermal oxidizers to destroy the fumes emitted by their treating ovens, containing phenolics and various types of solvents.

In addition to the burden of installing this equipment, the cost of fuel required to operate these oxidizers could double the annual fuel budget of these plants, threatening to force them out of business unless means were found to reduce these costs.

A laminate manufacturer in western New York State had coal-fired boilers which would require emissions controls or conversion to expensive fossil fuels, in addition to having to install and buy fuel for fume destruction.

These questions arose: could the heat discharged by the thermal oxidizers be recovered and used to provide plant steam? Could sufficient heat be produced to carry the entire plant load?

A study was made: it was found that thermal oxidizers with sufficient capacity to destroy the fumes generated by the plant could also generate enough waste heat to supply the needs of the entire plant throughout the year, provided that the waste heat boilers were designed to recovery the heat efficiently. This plant was designed and built Combustion Equipment Associates, and operated under contract from 1972 to 1979, after which the owner took over the operation.

THE NEW YORK PLANT

This plant had a favorable balance between the volume of fumes to be destroyed and the plant steam requirements: the heat generated by the thermal oxidation was sufficient to produce the steam and turbine power required by the plant, and vice versa. In addition to the heat loads for treating ovens and laminate presses, paper manufacture used large quantities of low pressure steam and could condense turbine back pressure steam.

The facility was designed to handle a maximum of 125,000 CFM of treater exhaust fumes at 200 F, containing phenolic resins, ketones, toluene and other solvents. A schematic is shown in Figure 1. Provision of five Thermal Oxidizer modules with four boilers and variation of furnace temperature gave the flexibility needed to accept all fumes while delivering all steam needed simultaneously. Each boiler has a capacity of 45,000 lb/hr of 150 psig steam. They were custom-designed by International Boiler Works with an optimum combination of finned and bare surface on

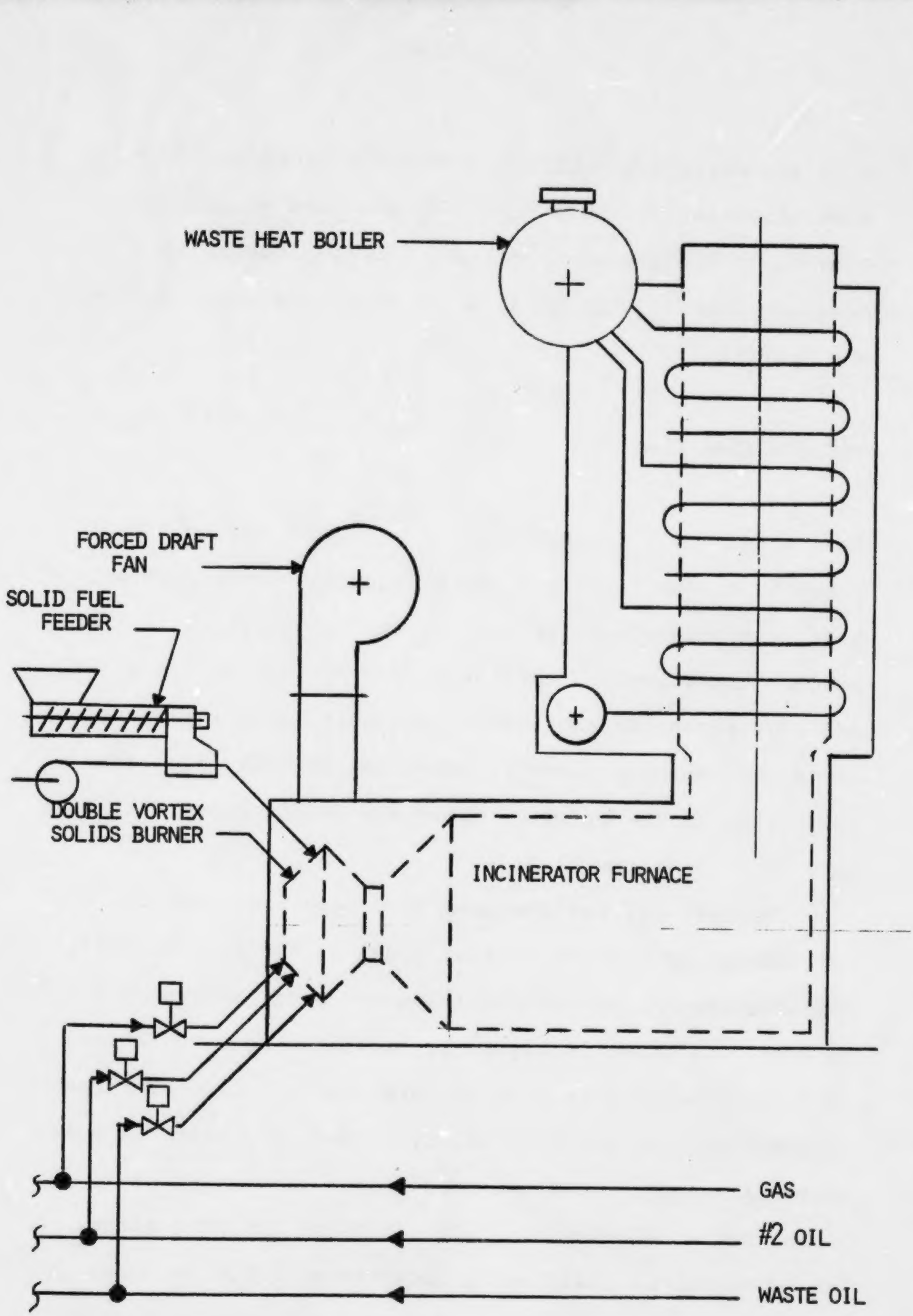

WASTE HEAT BOILER
FORCED DRAFT FAN
SOLID FUEL FEEDER
DOUBLE VORTEX SOLIDS BURNER
INCINERATOR FURNACE
GAS
#2 OIL
WASTE OIL

FIGURE 1 - ELEVATION OF FUME INCINERATOR WITH STEAM GENERATOR

the boiler and economizer to assure maximum thermal efficiency. Average monthly data showed that the steam generated represented over 90% of the heat supplied in the fuel, assisted by the temperature and solvent content of the fumes.

The burners were designed to burn gas, fuel oil and waste oil simultaneously and optionally. A newly-developed Double-VortexTM burner was installed in one furnace to permit burning shredded plastics, wood and paper. A two-stage shredding facility was installed to handle the tough phenolic scrap and the paper and canvas used to make laminates. Waste wood, battery cases and rubber tires were brought in and shredded for needed energy, in addition to plant scrap.

The fuel embargo was declared just after the plant was started up. Number 2 oil was allotted in accordance with usage during the previous year: this created a problem for this plant which had been burning coal. A search for alternate fuels was rewarded with discovery of a several million gallons of waste oils stored in the region, and consumed that winter, after processing by Chemtrol. Some of these wastes contained up to 5% halogens. A system was developed to inject caustic into the fuel as it was fed to the burner, which reacted with the chlorides within the flame envelope. The rate of injection was adjusted so that essentially no HCl was emitted from the boiler stack. The boiler tubes condensed salts which were water-washed off on weekends. About three million gallons of miscellaneous waste fuels were burned during the winter of 1972/73. The monitoring of chlorides in the boiler stack was labor-intensive, hence was discontinued in subsequent years when sufficient low-chloride wastes, (under 0.5%), became available.

THE PENNSYLVANIA FACILITY

Other laminate plants, without paper manufacturing, did not have as favorable a fume/steam balance. After extensive studies of the fume, thermal and power requirements of a Pennsylvania laminate manufacturer, CEA developed and offered a more sophisticated heat recovery system, with a similar contract to design, build and operate the facility, which would destroy treater oven fumes, aqueous and solvent wastes, and generate all processing heat as well as co-generate power up to 500 KW.

Fume/load balancing was harder to accomplish here: steam presses produced erratic fluctuations in steam demand, seasonal load varied due to loss of plant heating, weekend loads fell sharply. If fume flow was reduced, cold air would have to be used to generate steam, with a severe loss of efficiency. Figure 2 shows the variation of monthly

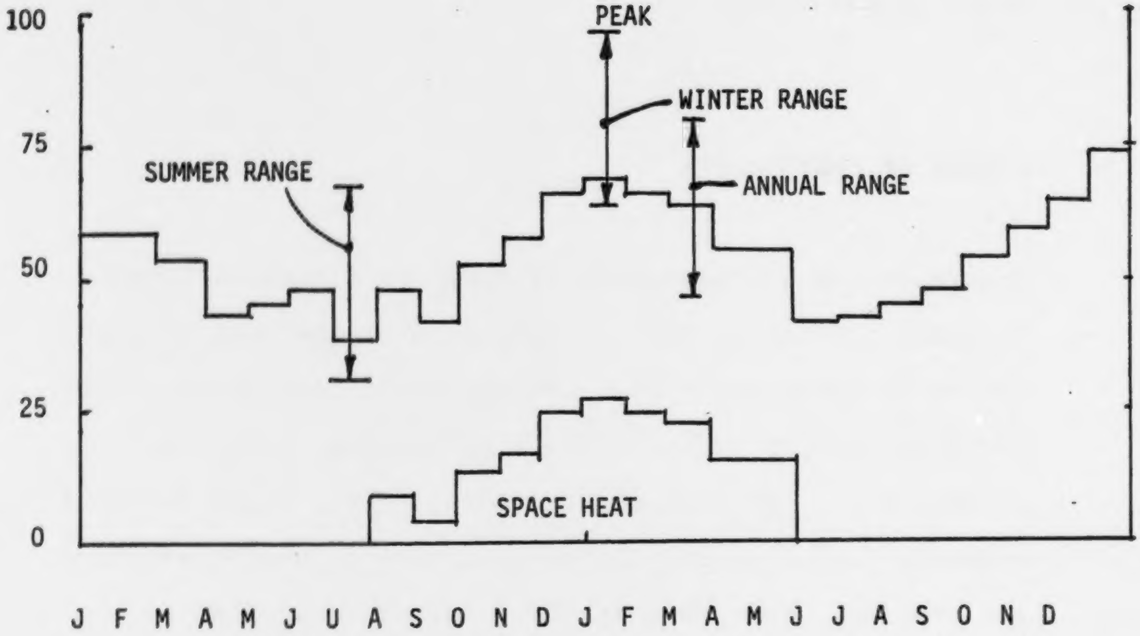


FIGURE 2 - DAILY AND SEASONAL VARIATIONS IN STEAM DEMAND OF LAMINATE PLANT.

average steam load and the range of daily steam loads for a laminating plant. The steam turbine could be driven from the 450 psig steam, discharging to the 150 psig processing steam mains. Additional power would be produced by expanding to the 20 psig mains which heating and drying needs of the plant.

DESIGN OF FUME SYSTEM

The layout of the equipment is shown in Figure 3. Fumes from six treating ovens are carried over the roof through sprinkler-protected ducts. Forced-draft fans are provided for each module, to force the fumes through the fume pre-heater to the Thermal Oxidizer burner. Draft controls maintain duct pressure slighly negative to draw fumes from the treaters. Induced-draft fans, draft-controlled to maintain furnace pressure slightly negative, pull the combustion gases through the furnace, waste heat boiler and fume preheater, discharging to the stack.

DESIGN OF THE STEAM AND POWER SYSTEM

The steam schematic is shown in Figure 4. A steam pressure master-controller maintains 450 psig steam pressure to

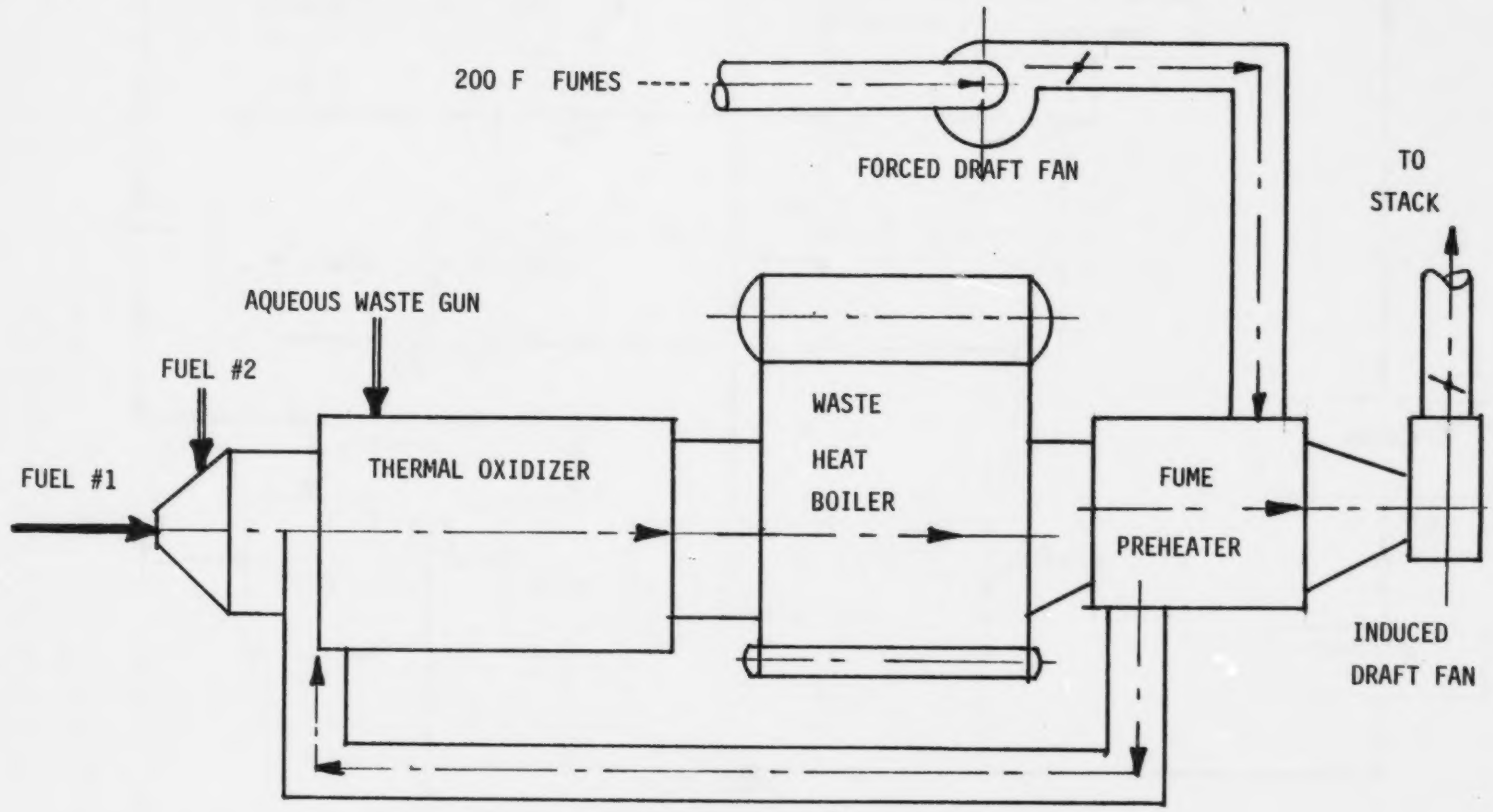

200 F FUMES
FORCED DRAFT FAN
TO
STACK
AQUEOUS WASTE GUN
FUEL #2
FUEL #1
THERMAL OXIDIZER
WASTE
HEAT
BOILER
FUME
PREHEATER
INDUCED
DRAFT FAN

FIGURE 3 - LAYOUT OF SYNTHANE FACILITY SHOWING PRECOMBUSTOR, FURNACE, BOILER AND FUME PREHEATER.

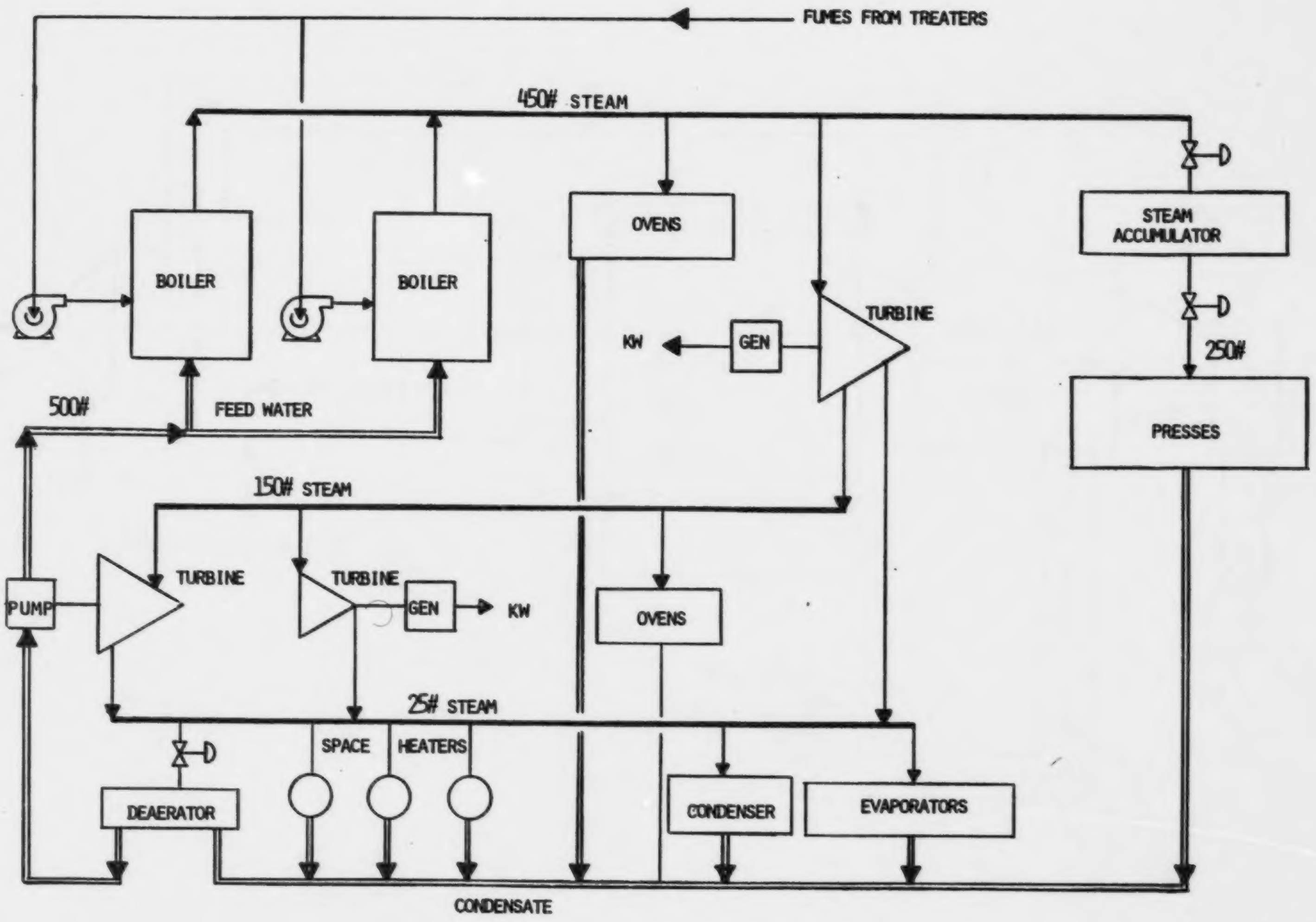

FUMES FROM TREATERS
450# STEAM
BOILER
BOILER
OVENS
STEAM ACCUMULATOR
TURBINE
KW
GEN
250#
PRESSES
500#
FEED WATER
150# STEAM
PUMP
TURBINE
TURBINE
GEN
KW
OVENS
25# STEAM
SPACE
HEATERS
DEAERATOR
CONDENSER
EVAPORATORS
CONDENSATE

FIGURE 4 - STEAM SCHEMATIC OF FUME AND LIQUID WASTE-STEAM AND POWER GENERATION SYSTEM

serve the treaters, feedwater pumps and power turbine, while extraction, backpressure or reduced steam serves the 150 psig and 30 psig steam systems.

A steam accumulator was provided to absorb steam press peaks and assure steady supply of steam to the plant, while the Thermal Oxidizer was accepting fumes at constant flow. The output of the waste-heat boilers can be adjusted within the necessary range by varying furnace temperature from 1400 F to 2000 F, giving a turndown of over 3:1. On weekends or when treaters are down, the fume flow can be reduced to help match the steam demand. Figure 5 shows the variations in plant steam demand (43,000 to 71,000 lb/hr), and the constancy of steam pressure delivered (396 - 420 psig) in spite of these load swings.

The boiler gas outlet temperature was selected to be about 600 F to match process steam needs: a fume preheater was installed to recover this heat, delivering roughly 410 F fumes to the Oxidizer and 350 F stack temperature.

The facility was provided with three International Boiler Works boiler/preheater modules, one a full spare, equipped with Double-Vortex pre-combustors, which are well-suited to combustion of several fuels at once (see Figure 6). Prime fuel (0.5% sulfur #6 oil), waste oil, and waste solvents can be burned at any ratio and quantity up to boiler capacity, in two guns located in the pre-combustor. Wastes

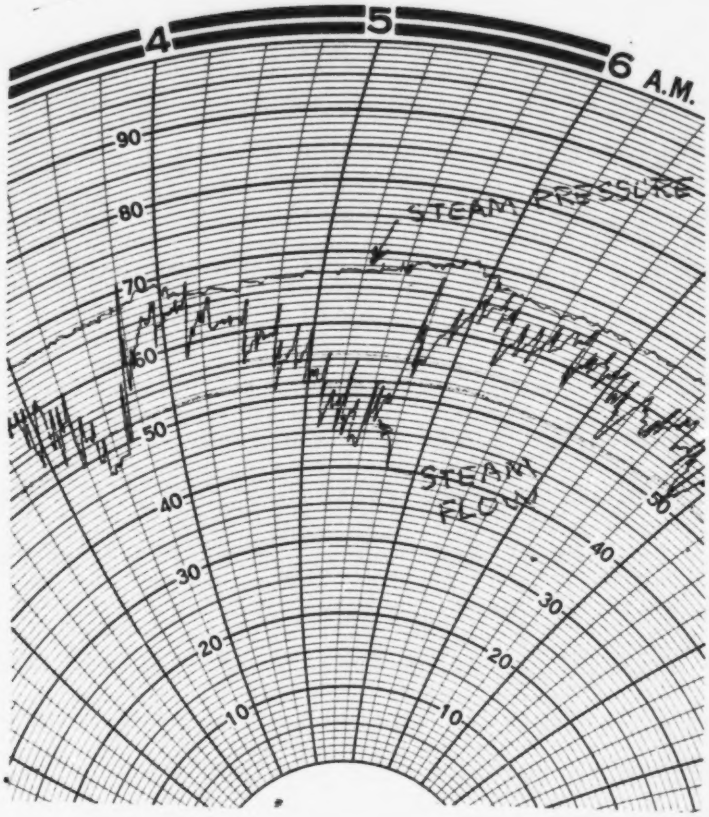
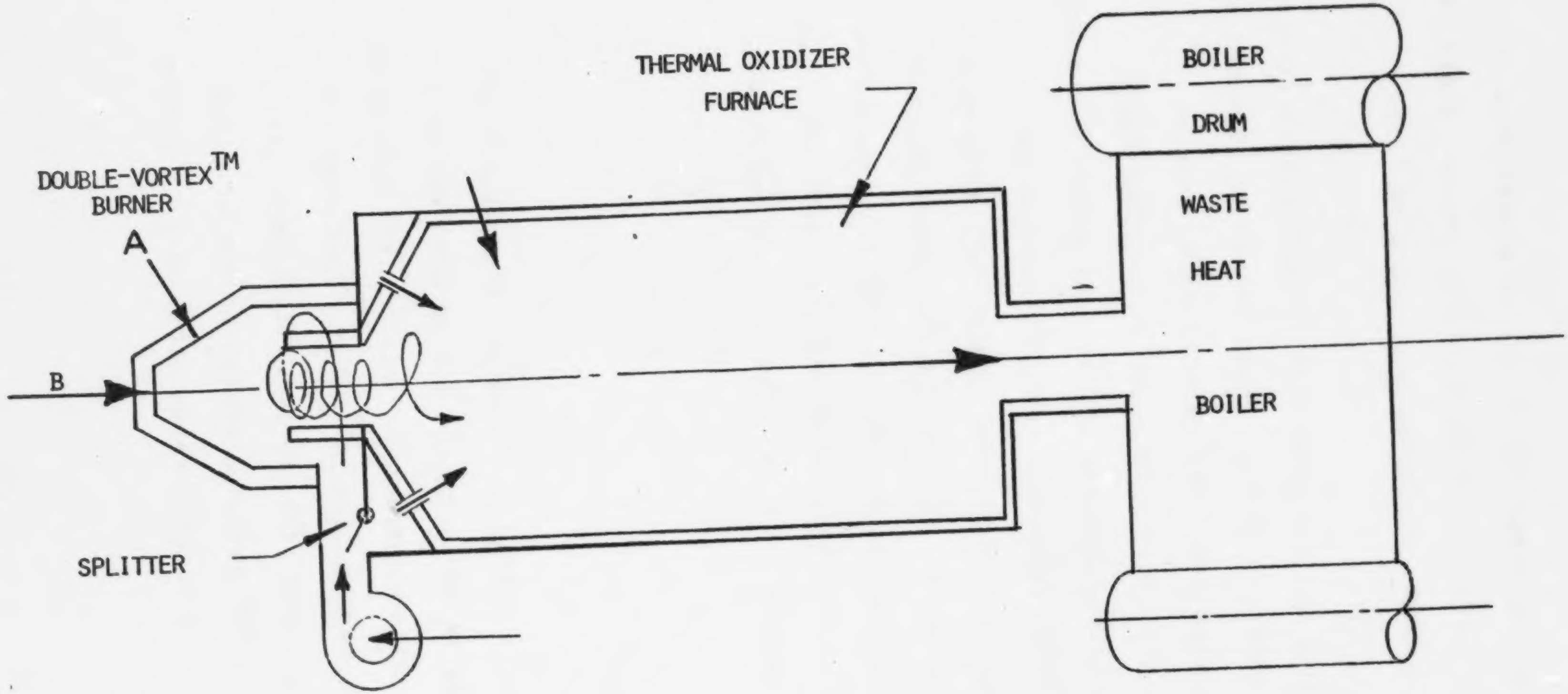


FIGURE 5 - VARIATION IN STEAM DEMAND AND STEAM PRESSURE


THERMAL OXIDIZER
FURNACE
BOILER
DRUM
WASTE
HEAT
BOILER
DOUBLE-VORTEX™
BURNER
A
B
SPLITTER

CROSS-SECTION OF THERMAL OXIDIZER
WITH DOUBLE-VORTEX
PRE-COMBUSTOR

FIGURE 6 - DOUBLE-VORTEX^{tm} PRECOMBUSTOR AND THERMAL OXIDIZER

containing up to 95% water can be burned either through a separate gun or blended with higher-value wastes, avoiding quenching of the flame or excessively reducing flame temperatures.

The facility was designed with as much flexibility as possible since fume and process steam demand is affected by marketing conditions and other developments, much as available fuels will vary. In order to tolerate fuels containing significant amounts of ash, the boiler tubes are arranged in straight lanes for ready inspection and periodic cleaning, and with access doors for cleaning and flushing. Provision was made for future installation of fabric filters for the stack gases in case this should be economically justified. Waste fuel ash is restricted to 1% ash and halogen content to 0.5% under present conditions.

THERMAL EFFICIENCY

Startup test data is listed in Table I. The temperature efficiency was 88% in spite of the 200 to 300% excess air associated with fume incineration. During 1977 when only #6 oil was burned, each gallon of oil produced over 125 pounds of 450 psig steam (89% thermal efficiency), as compared with about 100 pounds produced by the original boiler plant (72%). This remarkable efficiency is partly the consequence of burning 200 F fumes containing some combustibles.

BURNING LIQUID WASTES

The facility was originally permitted as a boiler burning #6 oil and 1500 gallons per day of waste solvents and aqueous wastes. The phenolic fumes and liquid wastes generated by the laminate plant were readily oxidized at the furnace temperatures normally maintained for steam generation (1400 to 2000 F, or 760 to 1100 C). Figure 7 shows how steam output is varied by changing furnace temperature.

After additional permits were obtained in 1978 to burn imported liquid wastes of similar types, a concerted effort was made to replace #6 oil with liquid wastes as much as possible: the ratio has been gradually increased until #6 oil has been totally eliminated as a fuel.

Figure 8 shows the total cost per million BTU of waste fuels for 1979 and 1980 compared with the price of #6 oil. The wastes are obtained mainly from well-known waste processing firms. Complete assurance of the chemical analysis and heating value of the wastes is required before they are accepted. The approximate amounts and types of liquid wastes burned at the facility are listed in Table II.

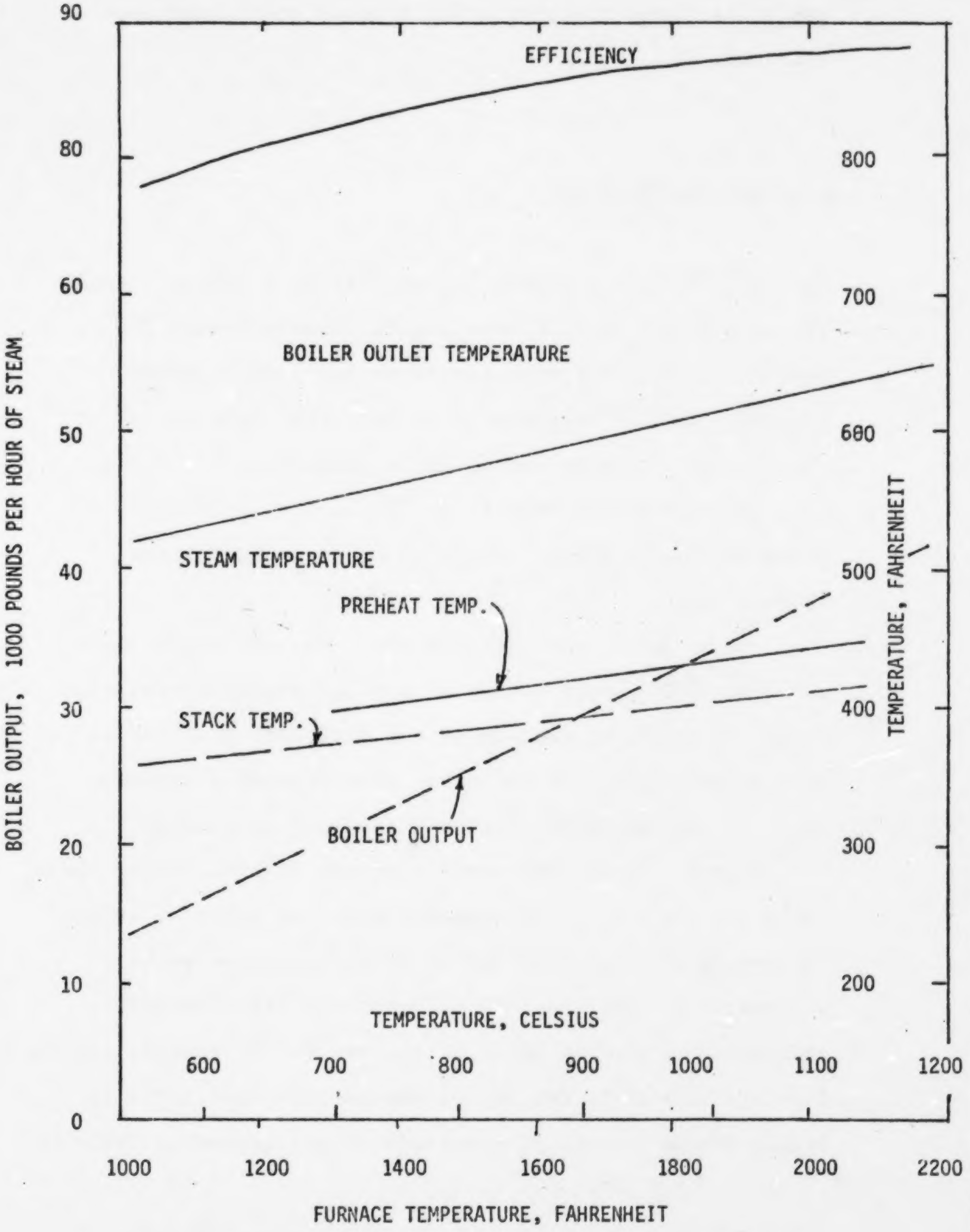


FIGURE 7 - VARIATION OF BOILER OUTPUT AND TEMPERATURES VERSUS OXIDIZER FURNACE TEMPERATURE

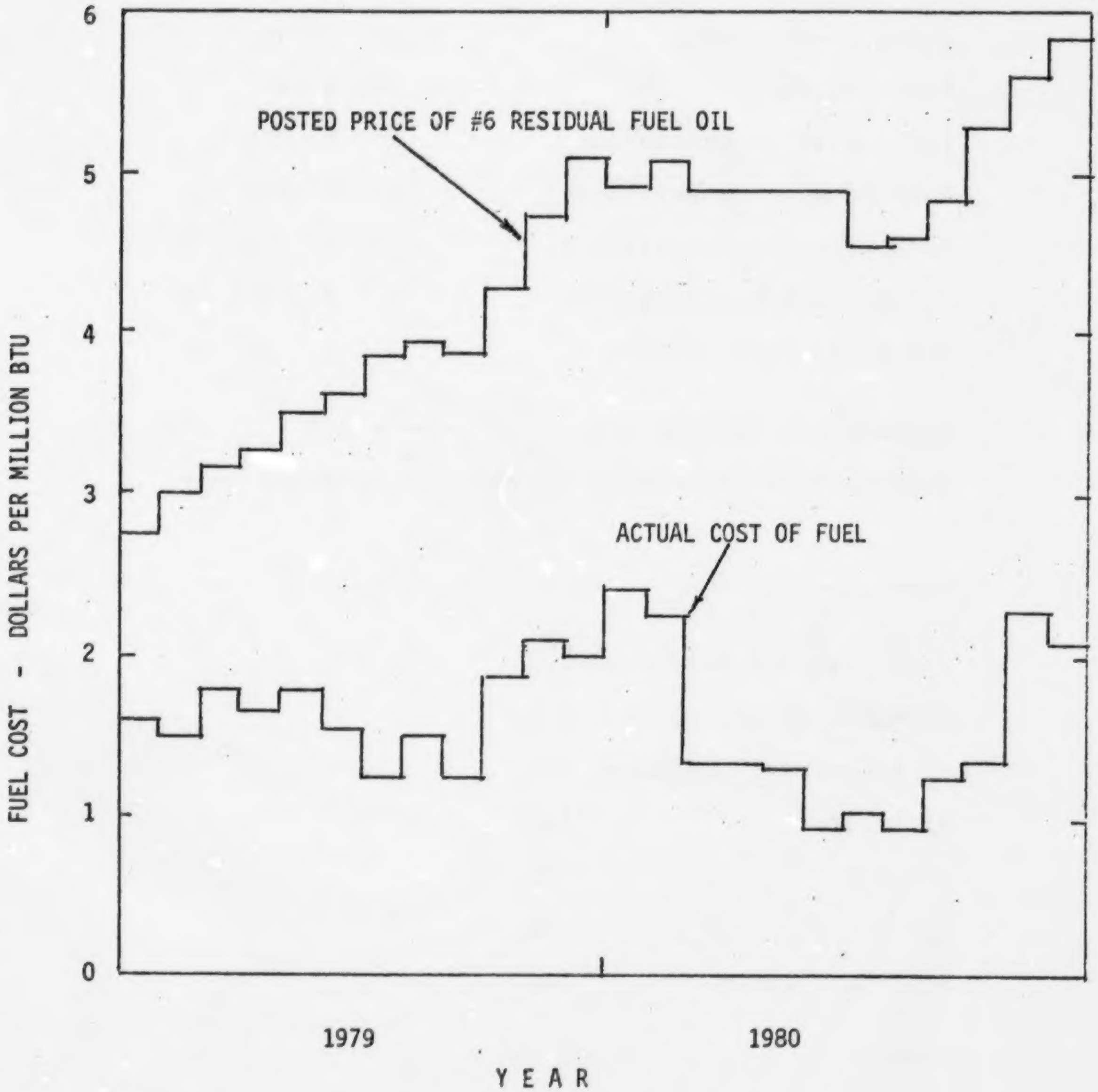


FIGURE 8 - ACTUAL WASTE FUEL COST VERSUS PRICE OF #6 FUEL OIL

TABLE I
TEST DATA OF THERMAL OXIDIZER HEAT RECOVERY UNIT

Number of Modules:	3	
Steam generation:	35,600 lb/hr	
Fume intake:	21,500 SCFM	
Fume inlet temperature:	190 F	(88 C)
Fume preheat temperature:	410 F	(210 C)
Oxidizer exit temperature:	1860 F	(1016 C)
Boiler exit temperature:	570 F	(300 C)
Stack gas temperature:	350 F	(177 C)
Temperature Efficiency:	$\frac{1860 - 570}{1860 - 410} = 89\%$	

TABLE II
TYPICAL ANALYSIS OF WASTES

AROMATIC HYDROCARBONS	35%
ALIPHATIC HYDROCARBONS	35%
ALCOHOLS	15%
KETONES	5%
ESTERS	5%
POLYMERIC RESINS	5%
DENSITY	0.95
BTU/GAL	100,000

In addition to the storage and pumping facilities provided in the original installation, new technology was developed to handle large volumes of variable material, including tanker unloading, prefiltering, testing, storage, mixing, pumping, piping and burner and burner management systems.

Using liquid wastes as alternate fuels requires continuous, proficient management of these highly variable materials, with frequent testing and constant attention to equipment and combustion. Under contract operation this burden is not placed on the personnel of the client, who must concentrate on his own business. The facility personnel are served by the home office in technical matters and marketing. The destruction of liquid wastes is handled under strict compliance with the regulations of the Resource Conservation and Recovery Act (RCRA) of November, 1980.

Operation of the facility requires careful selection of acceptable waste liquids, coordination of receipt, storage and burning with the steam generation requirements of the customer. Maintenance needed by the equipment is relatively high, requiring scheduled shutdown for cleaning, replacement of worn parts, repair and replacement of refractory and cleaning of sediment from tanks. Personnel accustomed to conventional fuels and chemicals find that it takes time and training to adjust to burning fuels with widely varying properties, while providing reliable steam flow and pressure.

Conventional burner control hardware is not suited to burning of liquid wastes which can be expected to contain abrasive and sedimentary materials, such as paint pigment and plain old dirt. Pumps with critical clearances wear out quickly, as do conventional control valves used to meter fuel to the burners and burner nozzles, requiring frequent replacement or substitution of more suitable methods of pumping and control. Steam atomization is used except for the first startup.

COMPLYING WITH EPA/RCRA REGULATIONS

RCRA regulations require preparation of manifests for all shipments of liquid wastes, assuring cradle to grave supervision: this record-keeping assists in assuring all parties that the waste is as-described, and that it will be destroyed properly. EPA regulations require controls and alarms to prevent operation of the oxidizer under less-than-satisfactory conditions. The EPA/RCRA regulations call for 99.9% combustion efficiency and 99.99% destruction efficiency. The original draft stated that certain classes of liquid wastes may require 1000 C (1832 F) furnace temperature for 2 seconds with a minimum of 2% excess oxygen, and that wastes containing over 0.5% halogens may require 1200 C (2200 F) for 3 seconds with 3% minimum excess oxygen, unless the destroyer can demonstrate that his facility can produce the required destruction under other conditions. This proposal has been dropped, leaving the requirement for 99.99% destruction efficiency.

The time/temperature/oxygen relationship actually required depends upon the design of the equipment used. In principle, destruction requires a certain minimum temperature for each substance, after which destruction is rapidly increased with relatively small temperature increase. Increased oxygen concentration increases destruction, but above 2-3% oxygen the affect of more oxygen is reduced. Fume preheat improves destruction by assisting ignition. The most important factor in destruction, after temperature and oxygen requirements are satisfied is efficient mixing of gases and temperatures. Short-flame high-intensity burners, such as the Double-VortexTM burner shown in Figure 6, are very effective. The facilities described above were designed for 0.5 second retention at 1400 F, based on the 'rule of thumb' published in the Los Angeles regulations. It was demonstrated at the New York facility that the objectionable phenolic odor was eliminated at temperatures as low as 1200 F. However, Figure 9, based on results of

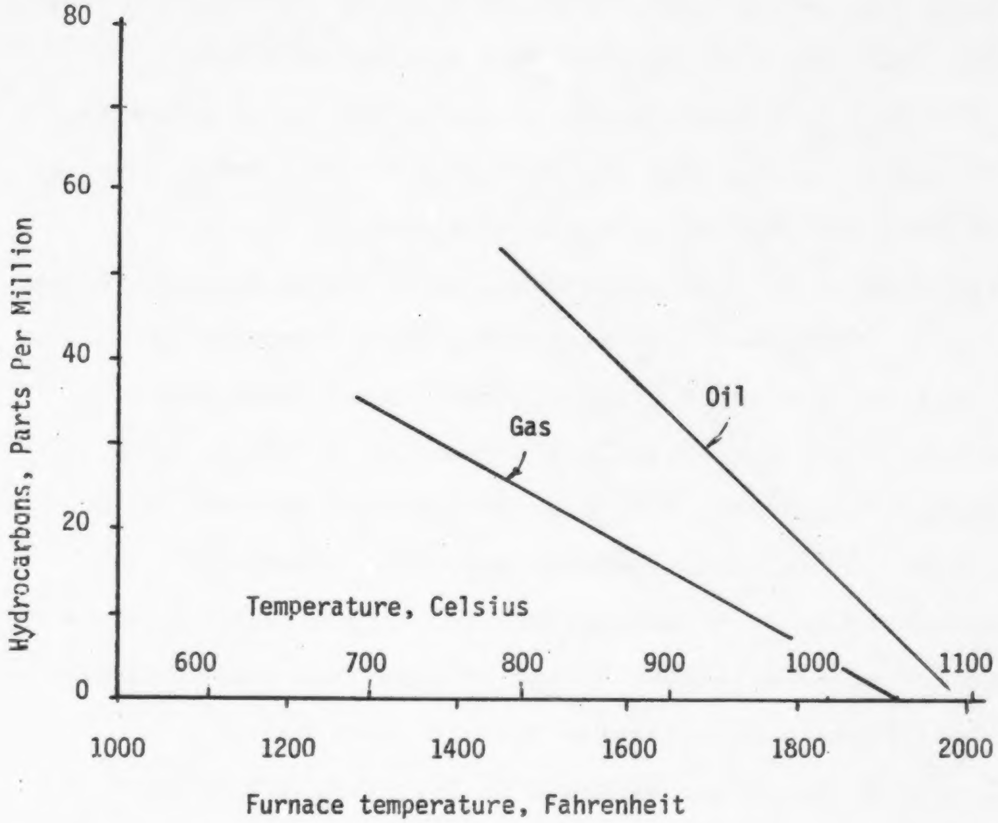


FIGURE 9 - Destruction of Hydrocarbons in Fuel Oil and Gas Fuel

stack tests of the thermal oxidizer, shows that the oil or gas fuel used produced hydrocarbons (HC) which were not destroyed unless temperatures exceeded 1400 F. Use of refractory good for service up to 2800 F (1550 C) has raised the potential furnace temperature, so that much higher destruction temperatures could be maintained if required. The amount of steam generated depends upon the furnace temperature as shown in Figure 7.

FACTORS AFFECTING DESTRUCTION EFFICIENCY

It is worth digressing at this point to discuss the factors which determine the residence time and temperature required to destroy particular liquid wastes.

Figure 10 shows results of tests published by Hemsath, Lewis and Thedki (1) on some typical solvents. The data falls on a straight line when the logarithm of the ppm remaining or the destruction efficiency is plotted versus residence or reaction time. The destruction was 99.9% at 0.2 seconds for the most difficult, Toluene, at 1410 F. Figure 11 shows the effect of increasing the furnace temperature, greatly reducing the reaction time at 1555 F. Another phenomenon is illustrated here: when the concentration had reached about 10 ppm out of an original 2000 ppm (99.5% destruction) time no longer had any effect. Probably due to deficient mixing: some of the material was able to pass through the reaction zone without attaining the necessary temperature. The shorter the reaction time the more material is likely to bypass.

Figure 12 shows some data generated in Dayton by Duvall (2) on the thermal decomposition (destruction) of pentachlorobiphenyl (PCB), a particularly hazardous material for the same reasons that it is hard to destroy: it is extremely stable. Here we see that destruction

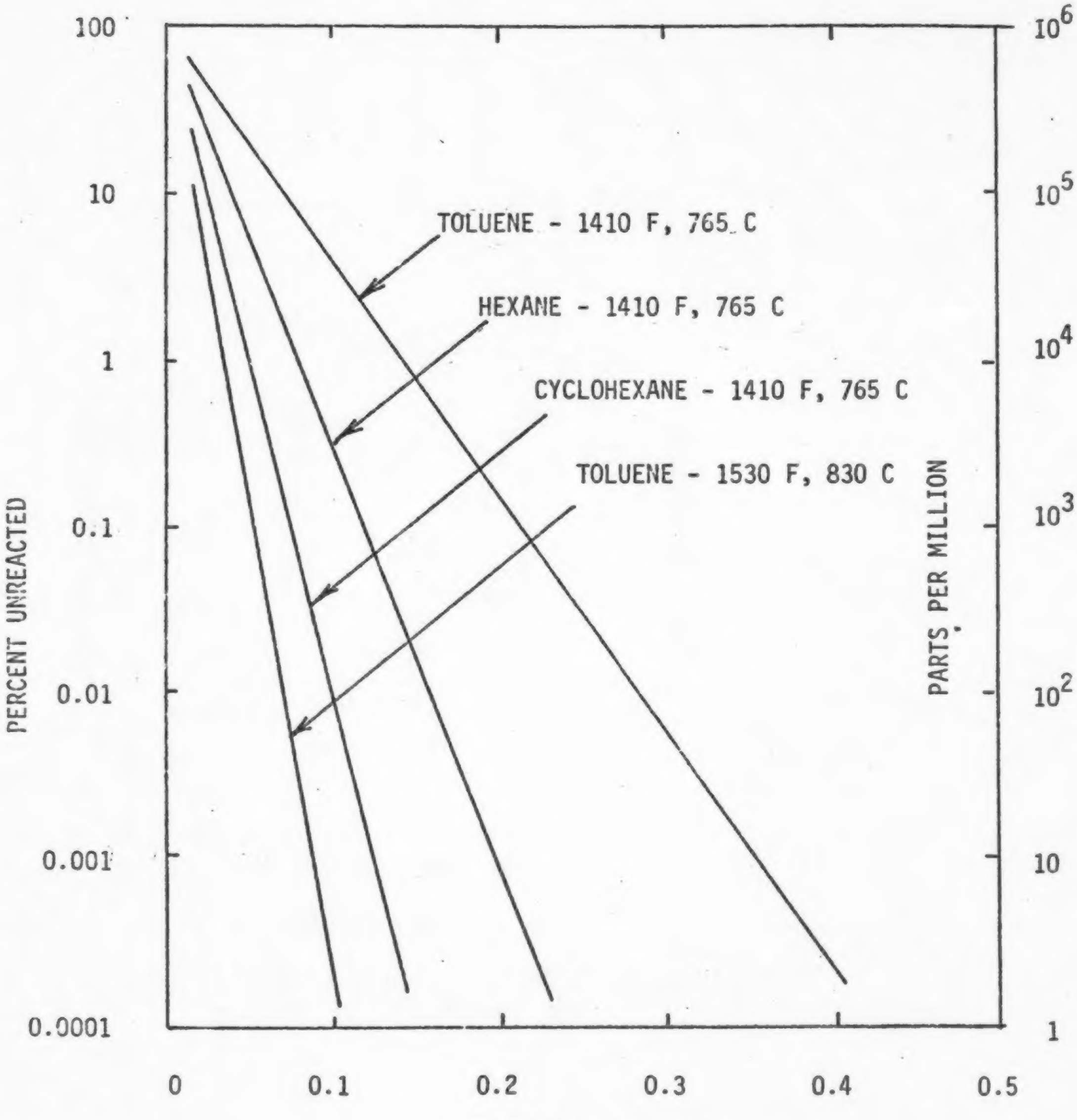


FIGURE 10 - DESTRUCTION OF SOLVENT HYDROCARBONS VERSUS RETENTION TIME AND TEMPERATURE.

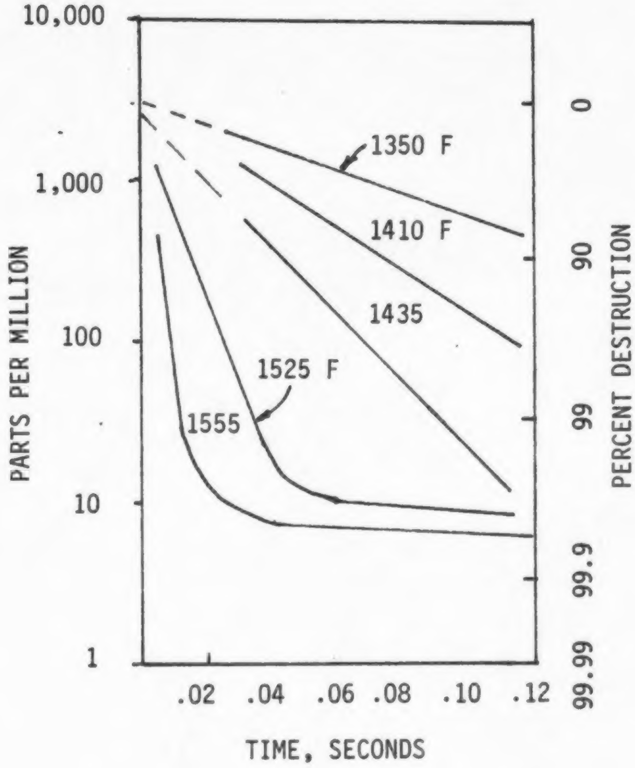


FIGURE 11 - DECREASE IN TOLUENE VERSUS TIME AND TEMPERATURE IN FURNACE

requires very high temperatures (about 1000 C) in a nitrogen atmosphere, yet it does take place. With 2.5% oxygen the destruction is complete at less than 850 C, and in air at about 750 C. The fume incinerator has an oxygen content close to that of air, hence even these difficult materials will be destroyed within the normal operating range of operating temperatures.

Figure 13 makes another point: some chlorinated materials are formed at lower temperatures and decomposed at higher temperatures. The temperature at which hexachlorobiphenyl is largely destroyed corresponds with the temperature at which penta-, hexa- and tetrachlorobenzene reach their maximum degree of formation, before they start to fall apart again. This illustrates the importance of maintaining temperatures over 800 or perhaps 900 C when these materials are present, such as in municipal incinerators.

Figure 14 shows destruction profiles for chlorinated materials, at one second retention time. A destruction efficiency of 99.99 was achieved for Biphenly and Dibenzo-p-dioxin at 750 C. Other data from Dayton shows that reducing the residence time to 0.5 seconds requires an increase in temperature of about 10 C, and increasing it to 2 seconds requires 10 C less.

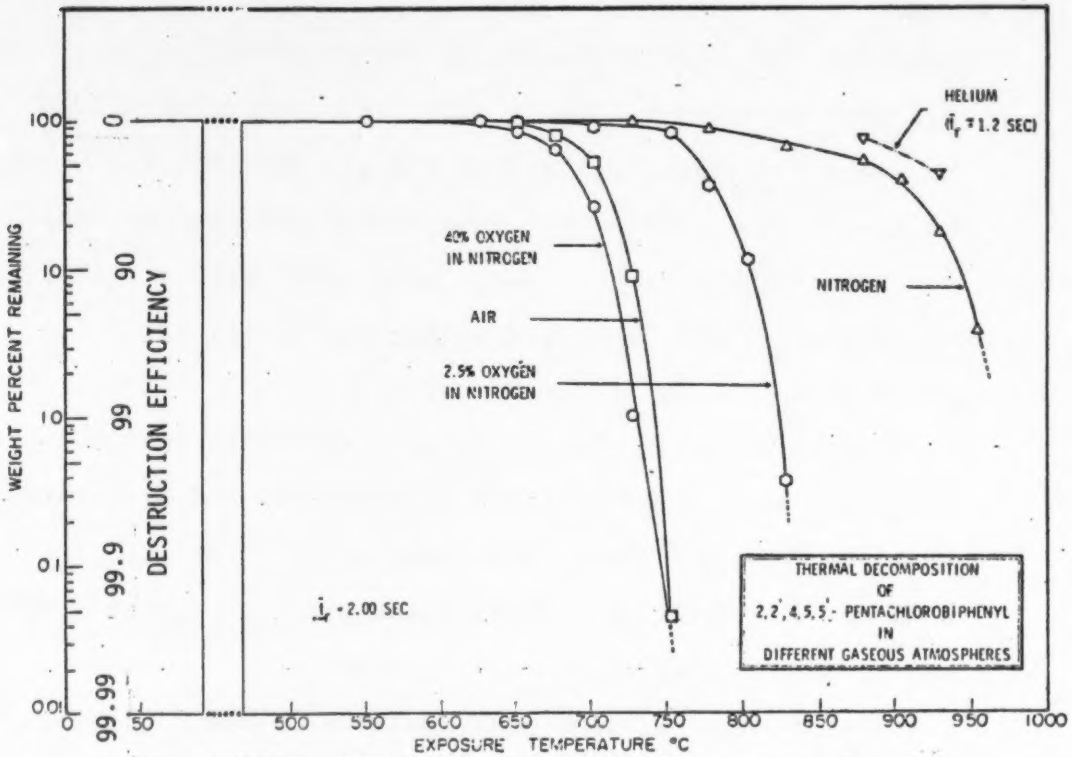


FIGURE 12 - EFFECT OF OXYGEN CONCENTRATION ON DESTRUCTION OF PENTACHLOROBIPHENYL

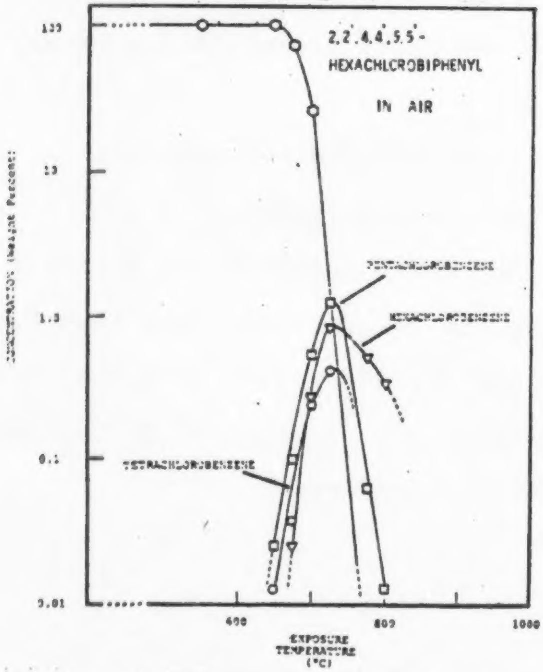


FIGURE 13 - DECOMPOSITION OF HEXACHLOROBIPHENYL

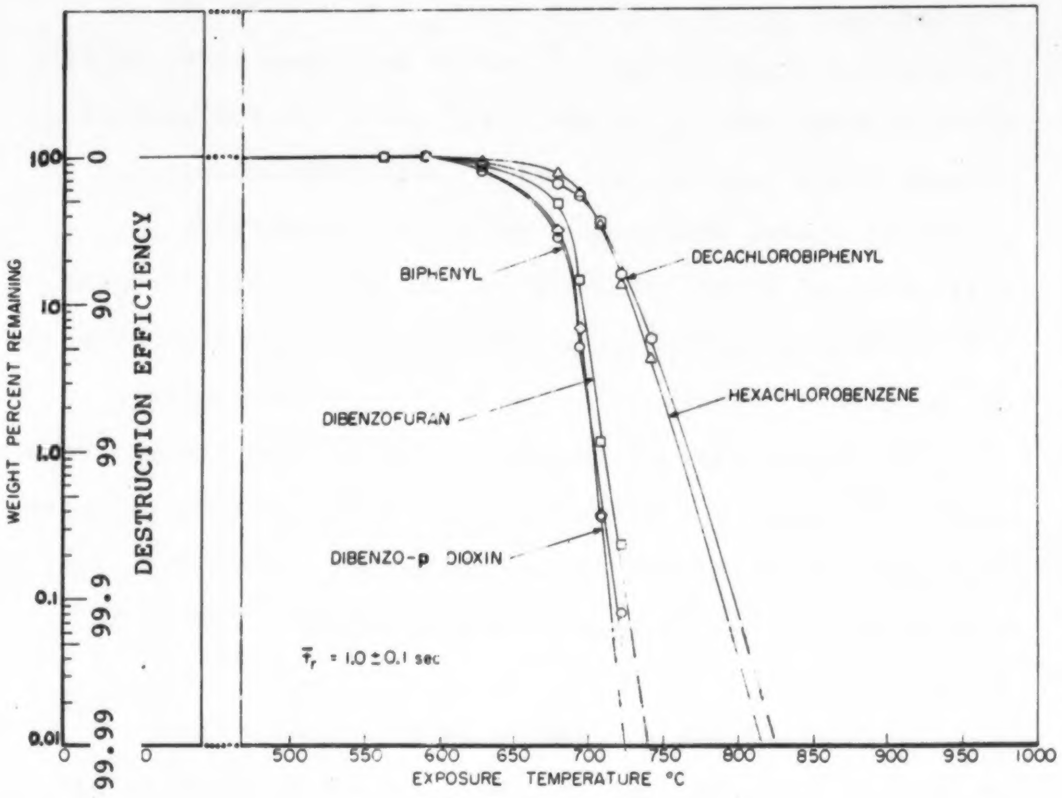


FIGURE 14 - Thermal destruction profiles for individual compounds in the combined samples. (3)

RELIABLE, EFFICIENT, ECONOMICAL OPERATION

The facility has been operated with better than 99% reliability since it was started in September 1976. In 1980 alone 953,000 gallons of waste oil and 2,030,000 gallons of solvent waste were burned, while generating 260 million pounds of steam. This indicates a steam generating efficiency of about 87% based on 1000 Btu/lb of steam and 100,000 Btu per gallon of liquid waste, taking into account the portion of wastes having about 140,000 Btu/gallon.

The actual cost of energy during the last two years is shown in Figure 8 While the cost of #6 residual oil rose from under $2 to almost $6 in this period, the actual cost of the waste fuels fluctuated within a range from $1 to $2.50.

Since the fumes are generated at a steady rate, efficiency of combustion is best achieved by maintaining steady fuel firing rates. The steam accumulator has proven to be effective in absorbing the short steam peaks so that the boiler controls could slowly accommodate the firing rate to basic changes in loading. Figure 5 shows the steady steam pressure which was maintained in spite of wildly fluctuating plant steam demand.

OPERATING PRINCIPLES

Operating principles are: keep a clean stack (monitored by the opacity indicator on the stack, which sounds an alarm); produce reliable steam; take all fumes at all times; then, burn as much unreliable waste as possible, watching for flame-outs and other operating difficulties.

SUMMARY

These facilities demonstrate the value of designing flexible systems which anticipate future needs for disposal of liquid wastes as alternate fuels while providing economical, reliable, fuel-efficient, safe generation of heat and power in an environmentally acceptable manner. They also show that contract operation by the designer/builder permits techniques and facilities to evolve optimally to suit changing conditions. They are an outstanding implementation of the philosophy expressed by the Resource Conservation and Recovery Act.

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OBJECTIVES OF AN EFFICIENT LIQUID WASTE-TO-ENERGY PLANT

- Minimize costs of waste disposal and emission controls
- Reduce fuel costs: use wastes as alternate fuels
- Produce power from heat
- Follow fume and steam load variations
- Single responsibility for design and operation
- Incentives for innovation and skill

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PROBLEMS IN COMBINING THERMAL DESTRUCTION WITH HEAT RECOVERY

- Inflexible rate of fume generation
- Variably of daily, and seasonal steam demand
- Match of incineration heat with steam demand
- Dependence of turbine output on LP steam demand
- Simultaneous combustion of multiple fuels
- Complete combustion of high-water wastes
- Adequate retention time and temperature
- Ash and halogen contents of some wastes

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METHODS USED TO ACHIEVE EFFECTIVE CONVERSION OF ENERGY

- Follow load and permit maintenance with Modular thermal destruction/heat recovery units
- Vary furnace temperature to control heat output
- Store heat with hot water or steam accumulators
- Cut costs by cogeneration of power
- Use multi-fuel combustors to burn liquid wastes
- Select wastes which can be burned within permissible emission levels
- Install flexible dirt-resistant storage and pumping and control systems
- Central responsibility to accept wastes and assure reliable operation of the facility

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REFERENCES

1. Hemsath, K.H., Lewis, F.M., Thekdi, A.C., "Effects of Mixing and Temperature on Reaction Rates in Fume Incinerators," Proceedings of the ASME Incinerator Division, January, 1972.

2. Duvall, D.S., Rubey, W.A., and Mescher, J.A., "High Temperature Decomposition of Organic Hazardous Waste," Proceedings of the Sixth Annual Research Symposium, March, 1980 EPA-600/9-80-011

3. Duvall, D.S. and Rubey, W.A., "Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds," EPA-600/2-77-228, December, 1977.

SESSION 4

TECHNOLOGY SYMPOSIUM II

CHAIRMAN:

R. S. HECKLINGER
Charles R Velzy Associates, Inc.
Armonk, NY

DESIGN AND OPERATION UNIQUENESS OF EXTANT EUROPEAN SOON-TO-BE-AMERICAN THERMAL DESTRUCTION PLANTS

D. P. BROWN
Waste Technologies, Inc.
Little Rock, AR

ABSTRACT

It is this Author's opinion that the level of state-of-the-art of this specific technology is at least 10 years more advanced as compared to current U.S. industrial waste incineration practices. This paper attempts to reveal some of the unique designs, not practiced in the U.S., that have met and exceeded formidable European hazardous waste incineration standards.

This paper will also delve into the design standards that are unique as compared to U.S. practices. They follow:

- Rotary kiln destruction efficiencies
- Fludizing - "wet" rotary klinker plasma maintenance, and benefits
- Operation in the run-of-the-warehouse-mode as opposed to batch charging procedures
- Truth-in-measurement of temperature/residence times
- Megawatts from industrial waste - better on-line availability indices as compared to other U.S. power boilers
- Emission controls - not basic parameters but waste specific data in tail gases
- Residuals - borasilicate glass forms.

Additional minor discussion will be given to:

- Siting success because of design standards
- Test burn results required to verify design limits
- Needs for pretreatment of wastes

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THE INCINERATION OF CHEMICAL WASTES AT THE BAYER-LEVERKUSEN PLANT
- A CASE STUDY -

G. R. GOLDGRABEN and P. R. CLIFFORD
The Mitre Corporation
McLean, VA

H. W. FABIAN and M. SCHOEN
Bayer AG
Federal Republic of Germany

ABSTRACT

Bayer Incinerator No. 2 was designed for the disposal of "special wastes" containing more than one percent chlorine, phosphorus, sulfur, nitrogen, fluorine or silicon compounds in accordance with anti-pollution statutes of the Federal Republic of Germany. This incinerator will also, on occasion, handle wastes from other Bayer facilities or from customers of Bayer AG. The incineration system and its operation are described. The wastes treated in the incinerator as well as operating and maintenance characteristics are discussed. Emission data are provided. The accident which occurred in 1980 is described together with the operating changes which will be implemented when the incinerator is put back on line in 1981.

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BACKGROUND

The Bayer Incinerator No. 2 is located in Leverkusen, Federal Republic of Germany. The incinerator is located near a large chemical manufacturing complex employing more than 35,000 people. The complex produces a wide variety of inorganic compounds, organic compounds, and polymers.

The Bayer facility at Leverkusen annually produces about 500,000 tons of solid and liquid waste. Approximately 400,000 tons are noncombustible solid wastes which are disposed of by landfilling. About 55,000 tons are combustible liquids, solids, or paste-like wastes which contain less than 1 percent sulfur, halogens, or nitrogen, as well as some domestic wastes. These wastes are burned in Incineration Plant No. 1. Of the 45,000 tons remaining, about 20,000 tons are special chlorinated wastes which are burned in incineration ships about 30 to 50 nautical miles off the Dutch coast. The remaining wastes, approximately 25,000 tons of combustible liquids, solid, and paste-like wastes, are burned in Incinerator No. 2. These wastes contain significant amounts of sulfur, halogens, phosphorus, nitrogen, and silicon compounds. This Bayer incinerator will also, on occasion, handle wastes from other Bayer facilities or from customers of Bayer AG.

Incinerator No. 1 was commissioned by Bayer in 1967. Construction was begun in 1973 on unit number 2 in order to supplement the incineration capacity at Leverkusen. Incinerator No. 2 was designed for the disposal of "special wastes" (wastes containing more than 1 percent chlorine, phosphorous, sulfur, nitrogen, or fluorine) in accordance with German anti-pollution statutes. Incinerator No. 1 is incapable of properly disposing of these "special wastes" because it lacks sufficient flue gas cleaning equipment. Incinerator No. 2 was commissioned for regular service in November 1977 following a shakedown period beginning in 1976.

DESCRIPTION OF WASTES TREATED IN INCINERATOR NO. 2

The types of chemical wastes that are burned in incinerator No. 2 are shown in Table 1. Because of the large volume and wide variety of wastes that are treated at this facility, it is not possible to provide specific chemical or physical properties for each waste item; nor is it possible to describe each of the waste components individually. However, Bayer classifies the wastes in four categories:

- Halogen, nitrogen, sulfur, phosphorus, and silicon containing production wastes
- Toxic, spontaneously igniting, decomposing, and polymerizing wastes, as well as wastes generating strong odors
- Wastes of high reactivity which may react spontaneously with other wastes or have a strong corrosive effect
- Miscellaneous wastes consisting of minor quantities of highly variable wastes whose composition is unknown (Fabian, 1979).

TABLE 1

CHEMICAL WASTE BURNED IN INCINERATOR NUMBER 2

WASTE TYPE	SALTS OR BASES PRESENT IN WASTE	METALLIC COMPOUNDS PRESENT IN WASTE
Refuse mixtures	NaCl, Na_2SO_4	--
Distillation residues	NaCl, $CaCO_3$, KCI Na_2SO_4, K_2SO_4	Fe, Mg, Si, Cr Mn, Al, Cu, Sr, Ti
Amino aromatics	NaCl, NaOH	--
Chloraniline residues	NaCl, NaOH	--
Resin residues	Na_2SO_4	Cu
Nitronaphthalene-sulphonic acids	--	--
Aromatic $Cl\text{-}NO_3$ compounds	NaOH	Fe
Nitrophenol residues	NaOH	Fe
Colour distillation wastes	NaCl, Na_2SO_4, Na_2CO_3, KCI	Cu, Fe, Cr, Zn
Pharmaceutical wastes	P-salts, K-salts, NaCl, Na_2SO_4	Mg, Si, Fe
Isocyanates	NaCl, $FeCl_3$, Al-silicates	Fe, Al
Filter cakes	Kaolin, Fe-oxides	Al, Fe, Cr, Si
Cresol remains	NaCl, $N3_2SO_4$	--
Thiophosphorus acids	--	--
Perhalogen mercaptans	--	--
Returned materials (insecticides)	Diff. salts, carbonates	--
Mother liquors	Na_2SO_4, K_2SO_4, NaCl, KOH, NaOH, KOH	--
Cresol, thiocresol	--	--
ABS wastes	--	--
Chloroprene remains	Na_2SO_4, NaCl	--
Silicone remains	NaCl, NH_4Cl	Si

SOURCE: Fabian, H.W., M Schoen, and K. Capek, 1979. "Problems in the Incineration of Refuse from the Chemical Industry." International Ceramic Review. Special Issue on Refractories, 28, 198-203.

The wastes may be in liquid or solid form or may be containerized. Based on the experience with Incinerator No. 1, Bayer expected that approximately 14,000 tons of solids, 7,000 tons of liquid, and 4,000 tons of containerized wastes would be treated by Unit No. 2 each year. Operating experience has shown, however, that about 3,000 tons of solids, 13,000 tons of liquid, and 4,000 tons of containerized wastes are actually disposed of in the incinerator. The calorific value of the wastes varies from zero to about 40,000 kJ/kg (17,211 btu/lb.).

SYSTEM DESCRIPTION

Bayer developed four operating and design criteria for Incinerator No. 2. First the system had to be flexible so that it would not be affected by changes in the quantity or the composition of the wastes being treated. Second, the combustion spaces and heat recovery systems and their construction materials had to be designed to be resistant to damage by the flue gases. Third, all wastes had to be analyzed and classified prior to incineration. Fourth, the flue gas scrubbing system had to be designed so that pollutants would be removed to the degree specified in the permits regardless of the quantity of individual flue gas components and the ratios among them.*

The concept for Incinerator No. 2 was developed in collaboration with L & C Steinmueller, D-5270 Gummersbach. Steinmueller also was the design and construction contractor. Incinerator No. 2 has a design capacity of about 25,000 metric tons of "special wastes" per year and produces approximately 140,000 tons of steam. It requires an operating staff of about 35 persons including instrumentation and maintenance personnel. The capital cost in 1976 for the incinerator was DM 27,000,000 ($15,390,000).* The operating cost is about DM 10,000,000 ($5,700,000) per year. The average incineration cost, therefore, is about DM 400 ($228) per ton of waste. A schematic diagram of Incinerator No. 2 is shown in Figure 1. The unit consists of a waste bunker building, feed devices for solid pastes and liquid waste, a rotary kiln, a second combustion chamber (afterburner), a heat recovery boiler, an electrostatic precipitator, and a wet scrubbing system. The wet scrubber system is composed of an injection cooler, two rotary scrubbers, and one jet scrubber. Downstream of the scrubbing system are two heat exchangers, a suction blower, and a 100 meter tall stack. The stack has sensors and analyzers for measuring and recording the quality and quantity of the flue gas emissions.

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*H.W. Fabian, P. Reher and M. Schoen, "How Bayer Incinerates Wastes," Hydrocarbon Processing 58(4)(1979):183-192.

Ash, dust and slag from the kiln and the precipitator are deposited in a landfill adjacent to the incinerator. Scrubbing water is treated in a nearby biological wastewater treatment facility. The technical specifications for Unit No. 2 are presented in Table 2.

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*DM - Deutsche Mark
It is assumed that 1 DM = $0.57

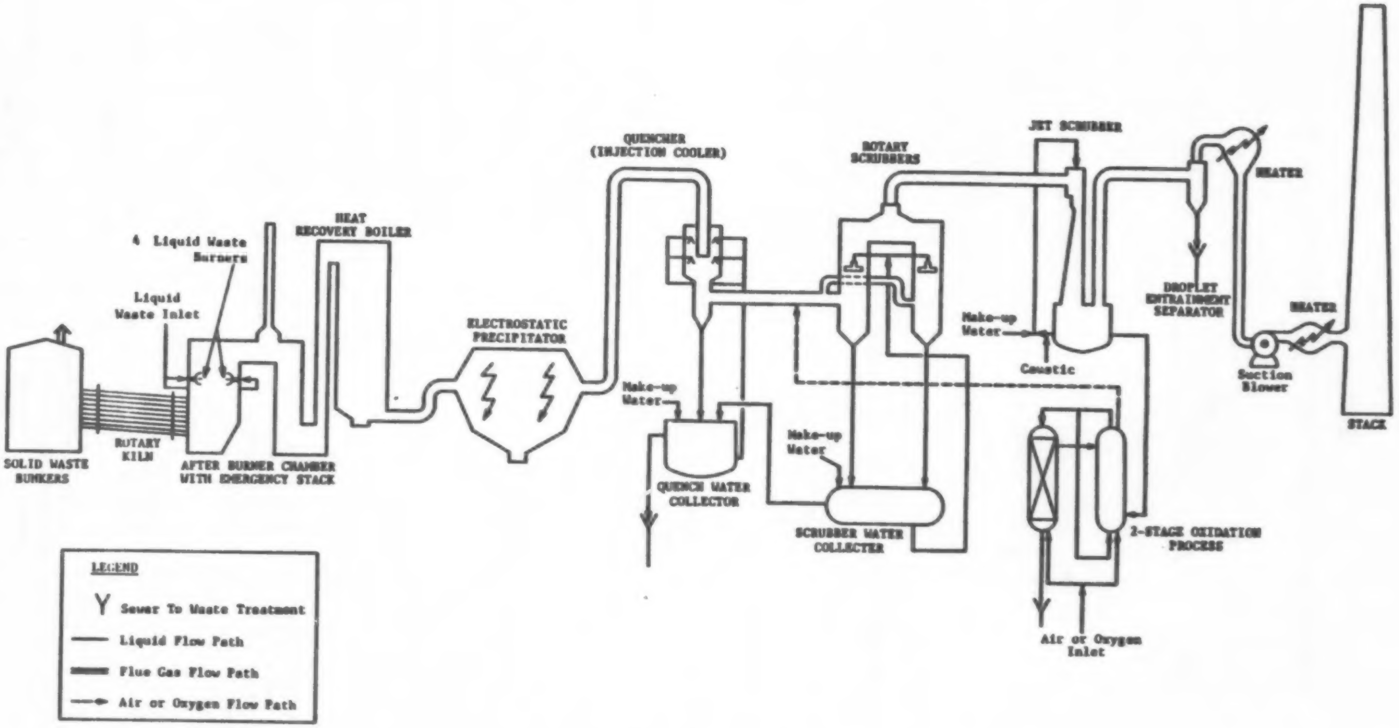
QUENCHER
(INJECTION COOLER)
JET SCRUBBER
ROTARY
SCRUBBERS
HEATER
HEATER
HEAT
RECOVERY BOILER
4 Liquid Waste
Burners
Liquid
Waste Inlet
ELECTROSTATIC
PRECIPITATOR
DROPLET
ENTRAINMENT
SEPARATOR
Make-up
Water
Caustic
Suction
Blower
Make-up
Water
STACK
SOLID WASTE
BUNKERS
ROTARY
KILN
AFTER BURNER CHAMBER
WITH EMERGENCY STACK
Make-up
Water
QUENCH WATER
COLLECTOR
SCRUBBER WATER
COLLECTER
2-STAGE OXIDATION
PROCESS
Air or Oxygen
Inlet
LEGEND
Y Sewer To Waste Treatment
Liquid Flow Path
Flue Gas Flow Path
Air or Oxygen Flow Path

FIGURE 1
SCHEMATIC DIAGRAM OF CHEMICAL WASTE INCINERATOR NO. 2

TABLE 2

TECHNICAL SPECIFICATIONS FOR INCINERATOR UNIT NUMBER 2

EQUIPMENT AND OPERATING PARAMETERS	EQUIPMENT COMPONENTS	CAPACITY AND OPERATING CONDITIONS
Bunker building		
Waste acceptance	4 chambers	200 m^3 capacity per chamber
Waste charging system	1 grapple	0.8 m^3 capacity
	1 plate conveyor	3-4 ton/hour
	2 slide gates	approx. 2-minute cycles
	1 charging ram	
	1 drum elevator	capacity 2-3 ton/hour
Rotary kiln		length 13.5 m (44.3 ft)
		diameter 3.5 m (11.5 ft)
		maximum thermal load 15 Gcal/hr (60 x 10^6 btu/hr)
Solid waste incineration (see above)		
Liquid waste incineration	various settling tanks	capacity 3-5 m^3
	tank farm	several tanks
	1 sustaining burner	capacity 300 kg/hr
Sludge incineration	1 injector	
Combustion air	1 blower	capacity 37,000 m^3/hr 21,755 cfm)
Cooling air	1 blower	capacity 5,400 m^3/hr (3178 cfm)
Flue-gas outlet temperature		1,100 to 1,200°C
Afterburner chamber		
Secondary combustion	various settling tanks	capacity 1-5 m^3
	tank farm	several tanks
	3 liquid burners	capacity 300 kg/hr per burner
	1 booster burner	capacity 50 kg/hr
Residence time		2-4 secs.
Flue-gas flow rate		40,000-50,000 m^3/hr. max (23,540-29,425 scfm)
		thermal load 20 Gcal/hr
		(76 x 10^6 btu/hr)
Flue-gas outlet temperature		1,200-1,300°C
Heat recovery boiler		
Heat recovery	4 ducts	20 ton steam/hr, 550 psi, 350° C
Flue-gas outlet temperature		300°C
Electrostatic filters		
Dry dust removal		max 20 kg dust/hr
Flue-gas scrubber		
Cooling and HCl separation	1 injection cooler	6-8 m^3 water/hr (1585-2114 gph)
Residual dust separation	2 rotary scrubbers	5-25 m^3 water/hr (1321-6605 gph)
Alkaline scrubber	1 jet scrubber	2-12 m^3 water/hr (528-3170 gph)
Sulfite oxidation	2 columns	
Exhaust air outlet Temperature		60°C
Waste-air heating	2 heat exchangers	
Suction blower	1 ducted-impeller blower	capacity 60,000 m^3/hr (35,310 cfm) drive rating 335 KW
Stack	insulated steel tube	
	instrumentation and recording devices	water-air outlet velocity 12-15 m/sec. (39-49 fps)

SOURCE: Fabian, H.W., P. Reher and M. Schoen, 1979. "How Bayer Incinerates Wastes." Hydrocarbon Processing 58(4):183-192.

PROCESS DESCRIPTION

Three separate charging systems are used for solid, liquid, and problem wastes in small containers. Solid waste is delivered in tipping lorries and collected in a sealed bunker building. There are four waste acceptance chambers in the building, each with a capacity of 200 cubic meters for a total capacity of 800 cubic meters. Bulky materials are crushed in an impact mill. The charging system for the crushed bulky solids consists of a charging hopper, which is fed by a grapple system; a continuously operating plate conveyor belt below the charging hopper, which moves the wastes into a drop chute and deposits it on an inclined sliding grate; and an inclined chute leading into the rotary kiln.

Liquid waste is delivered to the facility in sealed settling tanks having capacities up to 10 cubic meters. The liquid wastes may be either incinerated directly from these settling tanks or placed in storage. The storage capacity is 1100 cubic meters consisting of six tanks of 50 cubic meters, one tank of 300 cubic meters, and one tank of 500 cubic meters. Liquid waste is transported to the incinerator either by pumps or under nitrogen pressure. Wastes of low calorific value are atomized together with wastes of high calorific value in multiple fuel burners and are incinerated. Atomization can be accomplished either with compressed air or with steam. The liquid wastes may be fed to any one of five burners. One burner is on the face side of the rotary kiln and four burners are in the afterburner chamber. If the temperature drops below 1050°C, one of the burners in the afterburner chamber--the booster burner--may be fired with natural gas in order to support the main burners.

The facility also contains a system for directly charging small containers of solid, paste and liquid waste to the incinerator. This system consists primarily of an elevator, a roller conveyor, a lock with two sliding brakes and a tilting table from which the small containers enter the rotary kiln.

The rotary kiln is 13.5 meters (44.3 feet) in length, has a diameter of 3.5 meters (11.5 feet) and a maximum thermal load of 15 gigacalories (60×10^6 btu) per hour. It has a ceramic refractory liner of about one-quarter of a meter thickness, making the inner diameter approximately 3 meters. The kiln is inclined 3 percent toward the outlet end. The internal temperature of the rotary kiln is approximately 1200-1300° C with the hottest zone located between 7 and 11 meters from the inlet end. The residence time of the waste in the kiln is about one and one-half hours. The average rotating speed during operation is approximately 9 revolutions per hour; however, the speed is infinitely variable between 7 and 24 revolutions per hour.

Incinerator combustion air is injected into the rotary kiln inlet below the solid waste charging system. The air comes from the Bunker building at a rate of 40,000 standard cubic meters per hour (23,540 scfm). A water-filled plate conveyor slag removal system receives slag from the discharge end of the rotary kiln. The afterburner chamber is approximately 9 meters (30 feet) in height and has an inner diameter of 4.1 meters (13.5 feet). The afterburner has two ducts, both of which are lined with high temperature ceramic refractories. Halfway up the first duct, there are four liquid burners with an average through-put of about 300 kg/hour per burner. These burners are distributed around the circumference of the duct. Under normal conditions the minimum temperature in the afterburner chamber is 1000° C. When burning polychlorinated compounds, a minimum temperature of 1200° C is maintained. The residence time in the afterburner chamber is normally between 2 and 4 seconds with a minimum residence time of 0.3 seconds required. For polychlorinated compounds the minimum required residence time is 1 second. Secondary air nozzles, which were installed above the burners for safety reasons, are used to supply additional combustion air if needed. The second duct acts as a particulate removal chamber and contains an ash collection space on the bottom. Ash is removed with a front-end loader at regular intervals through a large port on the duct.

The heat recovery boiler is an upright four-duct boiler which produces about 20 metric tons of steam per hour at 550 psi and 350° C. The flue gases enter the boiler at about 1200° C and are cooled to about 300° C in the boiler. The flue gas cleaning system was designed to remove sulfur dioxide, hydrochloric acid, nitrogen oxides; and dust and minor quantities of hydrogen fluoride, sulfur trioxide, and phosphorus pentoxide. In designing the system, it was assumed that the flue gases would contain an average of 10 grams of hydrochloric acid per standard cubic meter, 2.5 grams of sulfur per standard cubic meter, and 2 grams of dust per standard cubic meter. It was also assumed that multiples of these concentrations could occur under peak load. The quantities of hydrogen fluoride, nitrogen oxides, sulfur trioxide, and phosphorus pentoxide were considered to be of negligible significance for purposes of design. Most of the dust is removed from the flue gas by an electrostatic precipitator. The precipitator is approximately 90-95 percent efficient during most of the operating conditions encountered. Incineration of silicon-containing compounds causes the efficiency to drop to less than 30 percent. The electrostatic precipitator was placed upstream of the wet scrubbing apparatus so that heavy metals contained in the dust or precipitated with the dust cannot get into the scrubbing system where sulfates and chlorides could dissolve and interfere with the operation of biological wastewater treatment.

From the precipitator, the flue gas is passed to the quencher (injection cooler). There, the gases are cooled from about 300° C to between 60° and 70° C while removing the majority of the hydrochloric acid. The scrubbing and cooling water required for the quencher is recirculated, and evaporation losses are made up by 6 to 8 cubic meters (1585-2114 gallons) per hour of make-up water. The hydrochloric acid concentration in the scrubbing water leaving the quencher ranges from 2 to 5 percent.

After the injection cooler, the flue gases pass into two parallel rotary scrubbers, where they flow through a dense cloud of fine water droplets generated by two rapidly rotating paddle wheels. In the rotary scrubber, any residual dust or extremely fine dust is separated, as are sulfuric acid aerosols which can be generated in the injection cooler. The rotary scrubbers can remove a large percentage of the dust in the flue gas when the electrostatic precipitator is off-line or when dust quantities are too great for the precipitator to handle.

The flue gas then passes from the rotary scrubbers to the jet scrubber where a weakly alkaline solution is used to remove sulfur dioxide, residual hydrochloric acid, chlorine, and nitrogen oxides. Sodium sulfite and sodium bisulfite are produced by the reaction of sodium hydroxide with the sulfur dioxide in the jet scrubber. These sulfites have a high oxygen demand and are oxidized to sodium sulfate with oxygen gas, or air, at a temperature between 70° and 90°C prior to discharge to the wastewater treatment system.

From the jet scrubbers, the flue gas passes through a droplet trap, a heat exchanger, a second droplet trap, and a second heat exchanger. The droplet traps and the heat exchangers are needed in order to prevent condensation and corrosion in the stack, and to ensure proper dispersion of the waste gases in the atmosphere. Hot water for the heat exchangers is obtained from the heat recovery boiler. Approximately five tons per hour of hot water are required for reheating the flue gases. This is equivalent to about 35,000 metric tons of steam per year assuming an average of 7,000 hours of operation a year. After reheating, the flue gases pass through a 100 meter (328 foot) high insulated stack.

OPERATING AND MAINTENANCE CHARACTERISTICS

Incinerator No. 2 has been in operation since November 1977. Maintenance is routinely performed approximately twice a year at 3500 operating hour intervals. The maintenance is scheduled for fall and late spring or summer to avoid freezing problems during the winter. Routine maintenance principally consists of checking the refractory bricks and replacing them as necessary. Complete renewal of the brickwork is only required during the late spring or summer maintenance period and therefore, this maintenance shutdown lasts longer than the fall maintenance shutdown. Total downtime during the late spring or summer maintenance period is five to six weeks. Three to four weeks are required for actual maintenance work, and the remaining time is allocated to shut-down and start-up of the incinerator.

The first two sets of brick work in the rotary kiln were replaced after being in service between 5000 and 5500 hours. It is believed that the first set of brickwork failed because the expansion joints were too far apart. The expansion joints of the second lining were spaced closer together and their arrangement was slightly modified. The second lining failed as a result of excessive corrosion. The excessive corrosion was due to the necessity to burn more liquid waste in the kiln burner than originally planned. The system was designed to handle 7,000 metric tons per year of liquid waste but actually received 13,000 metric tons per year. The three burners in the secondary combustion chamber were working at capacity and the additional liquid refuse could only be handled by increasing the throughput to the burner in the rotary kiln. The higher liquid burning rate in the kiln produced excessive heat which accelerated corrosive attack on the ceramic bricks. The problem was solved by adding a fourth liquid waste burner in the afterburner chamber.

After correcting the problem, the incinerator operated for 7500 hours before it become necessary to replace the bricks again. The incinerator then operated for 3500 hours before being shut down for routine maintenance. It is anticipated that the kiln will log between 7500 and 8000 operating hours before it becomes necessary to replace the bricks again. Special bricks are available which would permit the incinerator to operate for between 10,000 and 11,000 hours before it would become necessary to replace the refractory brick lining. However, the increased cost of the bricks is greater than the savings achieved by the longer running time. In addition, the lengthened running time would result in a shutdown during the winter months. Therefore, Bayer chooses not to use these special bricks.

The electrostatic precipitator is shut down for cleaning four to six times per year. The cleaning is required because of an accumulation of silicon dust from the burning of organosilicon and

and chlorosilicon compounds. The cleaning operation takes between one and three hours, during which time the incinerator continues to operate. Since the flue gases by-pass the precipitator, there is an increase in particulate emissions during the cleaning period.

Another problem that was encountered was that of excess smoke emissions when burning containerized wastes. It was found that the oxygen supply in the rotary kiln is inadequate to ensure complete combustion of containers larger than about 15 gallons and their contents. Therefore, containerized wastes must be limited to 15 gallon sizes.

DISCHARGES AND EMISSIONS

Air Emissions

The components of the flue gas discharged to the atmosphere are listed in Table 3. The flue gas discharge is monitored for the components specified in the operating license. The organics content of the flue gas is measured by a standard test method on an irregular basis (approximately weekly). Short chain organic compounds (e.g., methane and chlorinated methanes), are measured by carbon adsorption and gas chromatography of flue gas samples.

Wastewater

Wastewater is discharged from the quencher, the rotary scrubbers, and the jet scrubber. The quencher cools the flue gases leaving the electrostatic precipitator, and also removes the majority of the hydrogen chloride in the flue gas. The rotary scrubbers remove

TABLE 3

EMISSIONS TO THE ATMOSPHERE FROM INCINERATOR NUMBER 2

COMPONENT	NORMAL DISCHARGE, mg/m^3 (std)	PEAK DISCHARGE mg/m^3 (std)	ALLOWABLE MAXIMUM, mg/m^3 (std)
SO_2	300	800	1250
NO_x	400	>2000	1000
HCl	50	100	100
HF	3	5	10
Dust	20	100	100
PCB	$<10^{-3}$	-	-
Total Organics	<15	-	-

SOURCES: Fabian, H.W., P. Reher and M. Schoen, 1979. "How Bayer Incinerates Wastes." Hydrocarbon Processing 58(4):183-192.

Seyfried, M. and M. Schoen, 1979. Engineer, and Head of Incinerator Plant No. 2, Bayer AG, Leverkusen, Federal Republic of Germany. October 1979. Personal Communication.

residual dust, fine dust, volatile metal compounds, and sulfuric acid aerosol from the flue gas leaving the quencher. The wastewater from the rotary scrubber and the quencher is combined and together their volume is 50 cubic meters per hour. The combined wastewater contains between 2 and 5 percent acid (HCl and H_2SO_4). The jet scrubber uses a weak alkaline solution to remove sulfur dioxide, residual hydrogen chloride, and nitrogen oxide from the flue gas leaving the rotary scrubbers. The wastewater volume from the jet scrubber is about 4 cubic meters per hour, containing 2 to 3 percent of sodium bisulfate and sodium sulfate. This solution is oxidized with oxygen to sodium sulfate in a two-stage facility and then mixed with the wastewater from the injection cooler and rotary scrubbers prior to discharge to a biological wastewater treatment facility.

Additional wastewater is generated when slag or ash is flushed from the system. Heavy metals in this wastewater are removed by precipitation with milk of lime followed by filtration.

Solid Waste

Dry solid waste is obtained from the electrostatic precipitator and from the bottom of the second duct of the afterburner chamber. This waste is collected and deposited at a solid waste disposal site. Wet slag, ash, and sludge from wastewater treatment are also disposed of at the solid waste disposal site.

EVALUATION OF PERFORMANCE

Reliability

Peroxides and spray cans have been burned in the incinerator without incident. Small waste containers (60 to 100 liters) containing solid, paste, and liquid production or laboratory wastes of widely varying composition and calorific value have caused problems. Dropping the containers into the rotary kiln, without emptying them, occasionally results in deflagrations with soot generation, and excess thermal and mechanical loading of the kiln refractories. This problem has been resolved through incinerator design modifications and process modifications which are confidential.

Drs. Schoen and Seyfried of Bayer, AG, Leverkusen believe that the incinerator operates very well and provides a satisfactory solution to the problem of hazardous waste disposal at their plant. It is their opinion that such a facility is only economical where a sufficiently large amount of waste is to be disposed of (i.e., at least 25,000 tons per year). The cost of flue gas cleaning would be prohibitive for a small plant. Even for a large plant, the economics are only made satisfactory by heat recovery. In addition, one of the primary reasons that the Leverkusen incinerator has operated as well as it has is through careful control of waste mixing and having a wide variety of wastes that receive appropriate handling. Free halogens can form during the incineration of halogen-containing waste, causing corrosion of the boiler and system components.

However, if sulfur oxide is present in the flue gas, the halogens are reduced to halogenides, which are not corrosive. Thus, by incinerating halogen-containing waste together with sulfur-containing waste, corrosion damage has been lessened in the Leverkusen incinerator. Such waste mixing may not be possible at a waste facility which has limited amounts and types of waste.

Bayer personnel also feel that the control of the waste mix is vital and that the producers of the waste must know the proportions of the components in the waste that they intend to send to the incinerator. The functions of the Waste Acceptance Department are considered critical for the proper operation of the incinerator. The department reviews information provided about the waste by the generating department and conducts its own studies to determine the optimum disposal method. If it is proposed that the waste be disposed of by incineration, the waste is delivered with a waste way bill that lists the quantity, number and type of containers, inspection code, and materials classification code. On the basis of the assigned code the waste is channeled to the appropriate collection point depending upon its compatibility with other wastes.

Accident History

On July 15, 1980 at 8:25 p.m., an explosion occurred in the No.2 incinerator plant. This was the first accident since the incinerator was commissioned. The explosion killed one worker, injured eight others, collapsed the inner walls of the bunker, and damaged other parts of the incineration plant. Based on an investigation of the accident, Bayer has reconstructed the probable sequence of events which may have occurred.

It is believed that containers of liquid chemical wastes were stacked in the waste bunkers near the rotary kiln of incinerator No. 2, awaiting incineration. An unanticipated exothermic reaction probably occurred in the containers. The heat from the reaction produced gases which escaped from the containers, expanded into the rooms, and seeped into the rotary kiln. Finally, the mixture reached the burner in the kiln and ignited. The resulting explosion collapsed the inner walls of the bunker and the accompanying steel framework. Extensive damage was done to other parts of the incineration facility at considerable distances from the rotary kiln.

Despite the recent accident, Bayer personnel believe that incineration, and their incinerator in particular, is an effective and reliable solution to the problem of hazardous waste disposal at their plant. Therefore, the incineration facility is being rebuilt, However, the facility will be rebuilt without a waste bunker building, with a free-standing rotary kiln, and with a modified procedure for handling solid wastes.

Incinerator No. 2 was put back into operation in December 1980. The rotary kiln, in a free-standing configuration, is expected to be put back in service by the end of 1981. Currently, only liquid wastes are being incinerated because only the after-burner chamber is being used. The incinerator is currently operating at a rate of about two metric tons per hour. This represents an annual rate of about 15,000 to 17,000 metric tons. During March 1980, Bayer disposed of 1400 metric tons of liquid chemical wastes in facility No. 2.

The bunker building will not be rebuilt. This building was originally built at the suggestion of government officials concerned about the potential odor problem. The feed room, in the front of the building, could allow a gas cloud to accumulate. Such a gas cloud may have caused the accident. Since the combustion air is drawn into the kiln from the bunker building, any gases built up in the feed room would probably also be drawn into the kiln.

When the rebuilding of the incineration facility is completed, solid wastes will once again be burned. Bayer has found that prior to the accident, the amount of solid wastes burned amounted to about 25 percent of the original design estimate. Because the amount of solid waste is so small, solid wastes will be containerized and charged directly to the kiln when it is put into service.

DESIGN CONCEPTS FOR LARGE SCALE ROTARY KILN INCINERATION AND ENERGY RECOVERY FACILITIES

T. L. RINKER
Koppers Environmental Elements
Baltimore, MD

ABSTRACT

The paper will review principal design concepts for large scale rotary kiln incineration facilities designed to handle a wide range of waste streams. The scope will include material handling, incineration, energy recovery and utilization, flue gas cleaning and residue handling components. Discussion of design concepts will be supplemented by comments and operating experience at major European regional hazardous waste management facilities.

ENGINEERED SYSTEMS FOR HAZARDOUS WASTE INCINERATION

Y. H. KIANG
Trane Thermal Company
Conshohocken, PA

ABSTRACT

Engineered systems for hazardous waste incineration can be defined as systems which are designed and developed, after extensive definition and evaluation of the problem for optimal disposal of a specific hazardous residue. The consideration will not only involve incinerator design, but also the possibility of waste heat and by-product recovery system design.

This paper discusses the basic methodology of engineering system design and development approach.

Also included in the discussion are examples which illustrate the usage of the engineered system approaches. The examples are:

1. The incineration of vinyl chloride monomer plant wastes.
2. The energy requirement study for the incineration of agricultural chemical plant wastes.
3. The design of an incineration facility for a chemical plant waste with wide composition variations.
4. The application of engineered system approach to a central hazardous waste disposal facility.

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Engineered systems for hazardous waste incineration can be defined as systems which are designed and developed, after extensive definition and evaluation of the problem, for optimal treatment of a specific hazardous waste. The consideration will not only involve the selection and design of the incinerator, but also include the possibility of minimizing energy requirement, waste heat and by-product recovery, and the potential of integrating the incineration system into process plant.

The design of engineered systems for hazardous waste incineration requires a coherent methodology to approach the problem. The key steps are summarized in Table 1. Each of these steps is described in detail below.(1)

1. Problem definition is used to broadly establish the goals of incineration systems. This should include, at minimum:
   A. The type or types of wastes to be treated in this system.
   B. The degree of destruction for these wastes.
   C. The guideline of air, water, and solid discharge requirement.
   D. The guideline for energy and by-product recovery, such as potential user of the recovered energy and materials.
2. Front end process engineering is the heart of the engineered system concept. It consists of the following steps:

Table 1

ENGINEERED SYSTEM METHODOLOGY

1. Problem Definition

2. Front End Processing Engineering

   A - Waste Characterization

   B - Process Requirement Definition

   C - Process Concept Development

   D - Process Design Calculations

   E - Process Control Philosophy Development

   F - Process Flow Diagram Preparation

   G - Preliminary Piping and Instrumentation Diagram Preparation

   H - Process Equipment Sizing

3. Technical Evaluation

4. Economic Evaluation

5. System Selection

A. Waste Characterization

More detailed analysis is performed to determine the physical form, chemical constituents, thermal ratings, and the incinerability of the wastes. The normal, minimum and maximum flow rates of the wastes are identified. The seasonal variations are defined for chemical constituents, thermal ratings and flow rates.

It must be noted that the incinerability determination derives from past experience and theoretical consideration. Pilot plant testing is necessary for new types of wastes.

B. Process requirement definition involves the determination of the measurable process design parameters - residence time, incineration temperature and excess air - in conjunction with a specific mixing pattern, the degree of destruction of the wastes(2,3), the air and water pollution control system requirement for clean flue gas and discharge water, and the feasibility and potential uses of recovery of energy and by-product chemicals.

C. Process concept development defines the alternative systems that can be developed to satisfy the waste and process requirement. The basic process design parameters are then selected based on the characteristics of the system and past experience. New wastes or new processes require pilot plant tests.

At this stage, wastes are grouped, based on their chemical constituents, physical properties, and compatibility, into several feed streams. The grouping of the waste is a very critical step. The consideration includes not only physical properties and compatibility, but also chemical constituents in conjunction with process requirement.

Process concept development is a prescreening step to determine the feasible systems. A schematic logical diagram of this prescreening step is illustrated in Figure 1.

D. Process design calculation involves material and energy balance for each alternative system. The hardware characteristics and limitations as well as process control philosophy, as defined in the next step, should be considered in the calculation.

E. Process control philosophy development is used to determine the minimal instrumentation and control requirement to achieve the waste treatment and process requirement purposes.

F. A process flow diagram is then developed as the result of previous work.

G. A preliminary piping and instrumentation diagram covering the basic process equipment and process control philosophy will then be developed from information obtained thus far.

H. Process equipment, such as incinerators, reactors, and scrubbers are then sized.

3. Technical evaluation is then performed to determine the advantages and disadvantages of all the alternative systems.

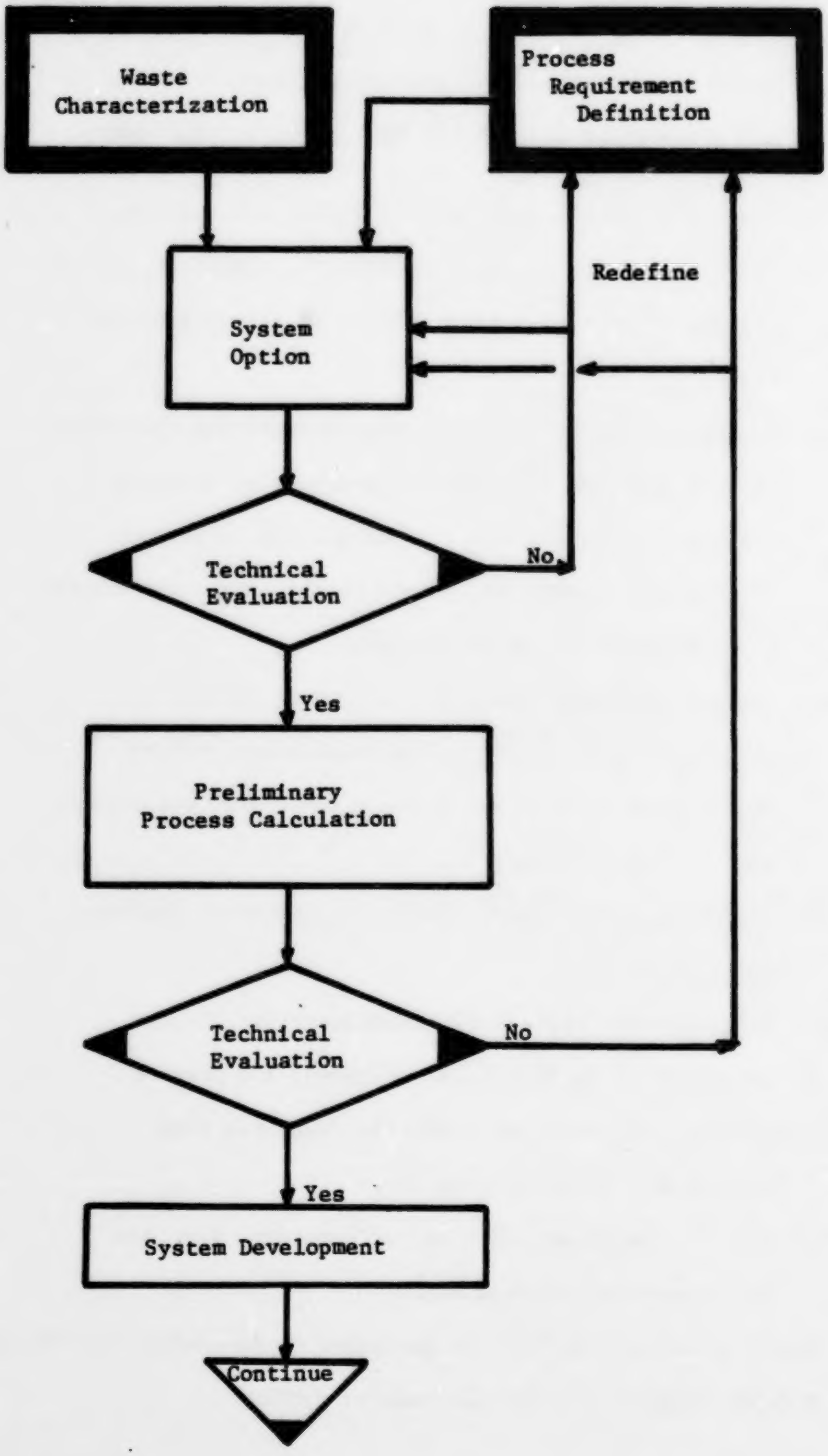

Waste
Characterization
Process
Requirement
Definition
System
Option
Redefine
Technical
Evaluation
No
Yes
Preliminary
Process Calculation
Technical
Evaluation
No
Yes
System Development
Continue

Figure 1. Process Concept Development

4. An economic evaluation is then performed to determine the comparative capital and operating costs of all the alternative systems.
5. System selection is based on the balance between the technical and economical evaluations.

This paper discusses four examples for the application of the engineered system approach to hazardous waste incineration.

EXAMPLE 1

Problem Definition

In a major manufacturing complex, the waste survey showed that there are over thirty hazardous liquid waste streams. The plant is interested in an incineration system to dispose of the wastes. The stack gases and waste waters from the incineration system must meet applicable environmental codes. Also, steam generation is preferred as the waste heat recovery means.

Front-End Process Engineering

A - Waste Characterization. After detailed analysis, it was determined that the waste liquids can be grouped into four different categories: organic, chlorinated organic, alkali organic, and aqueous wastes.

B - Process Requirement Definition. It was determined that pilot plant tests are required to evaluate the time, temperature and excess air requirement for waste destruction by a specific incinerator design. Waste heat recovery as steam is preferred; however, other means are also possible.

C - Process Concept Development. Based on the type of waste and heat recovery requirement, the fluid bed incinerator-boiler combination followed by venturi scrubber for air pollution control seems to be the better choice. However, after a closer examination of the wastes, two potential problems were identified. Firstly, the chloride in the wastes will form eutectic compound in the bed, which will then lower the melting point of the bed materials. Secondly, the varying composition of the wastes causes the change in composition of the salt mixture in the bed.(4) Thus, the incineration temperature must be lower than 650°C (1200°F) to take care of the eutectic point variations. At temperature lower than 650°C (1200°F), carboneous materials will be formed in the ash and carbon monoxide emission will be high, requiring afterburner and thus increasing fuel usage. Thus, fluidized bed incineration application was considered to be technically not feasible.

The second option is to use liquid injection incinerators. The optimal incineration temperature to dispose of alkali wastes is found to be between 870 (1600) and 980°C (1800°F).(5) The orientation of the incinerator chamber is usually in vertical downfired design. The temperature and downfired design are required to ensure the salts are in molten state and flow down the refractory wall into salt cooling chamber. This temperature selection is critical because too low a temperature will cause the salt to freeze on the walls and possibly block the incinerator discharge. Too high a temperature will produce alkali oxide vapor, which will react with refractory and cause refractory spalling.

Technically, there is no problem to design a liquid injection incinerator to meet pollution code requirement. However, the combination of alkali waste and waste heat boiler is not a proven technology. Thus, heat recovery for steam generation is not technically feasible. A request was sent back to the plant for changing heat recovery requirement. In the request, the waste heat source was identified: the water vapor saturated gas at 88°C (190°F). Only low temperature waste heat recovery applications are feasible. In response to the request, the plant came up with two process liquid streams to be heated to 60°C (140°F). These are ideal applications for alkali waste incineration systems.(3) Thus, the system illustrated in Figure 2 was developed.

D - Process Design Calculation. Based on the system described in Figure 2, material and energy balance calculation was performed. The calculation showed that only part of the organic and chlorinated wastes are needed to incinerate the alkali and aqueous wastes. Thus, a second system, the chlorinated hydrocarbon incineration and waste heat boiler system (Figure 3), was developed.(6)

Based on the two systems, the other steps of front-end process engineering are then performed.

EXAMPLE 2

Problem Definition

A vinyl chloride manufacturer has three types of wastes - two gaseous and one liquid. They want to install an incineration system to dispose of the wastes and recover waste heat as steam.

Front-End Process Engineering

A - Waste Characterization. The wastes were categorized as chlorinated liquid waste, high Btu chlorinated gaseous waste, and dilute gaseous waste.

B - Process Requirement Definition. The time, temperature, and excess air requirement for this type of wastes, based on a specific incinerator design, are well established. One special requirement imposed on this system is the reliability.

C - Process Concept Development. The basic process to handle this type of wastes is well established. Waste heat boiler application to chlorinated

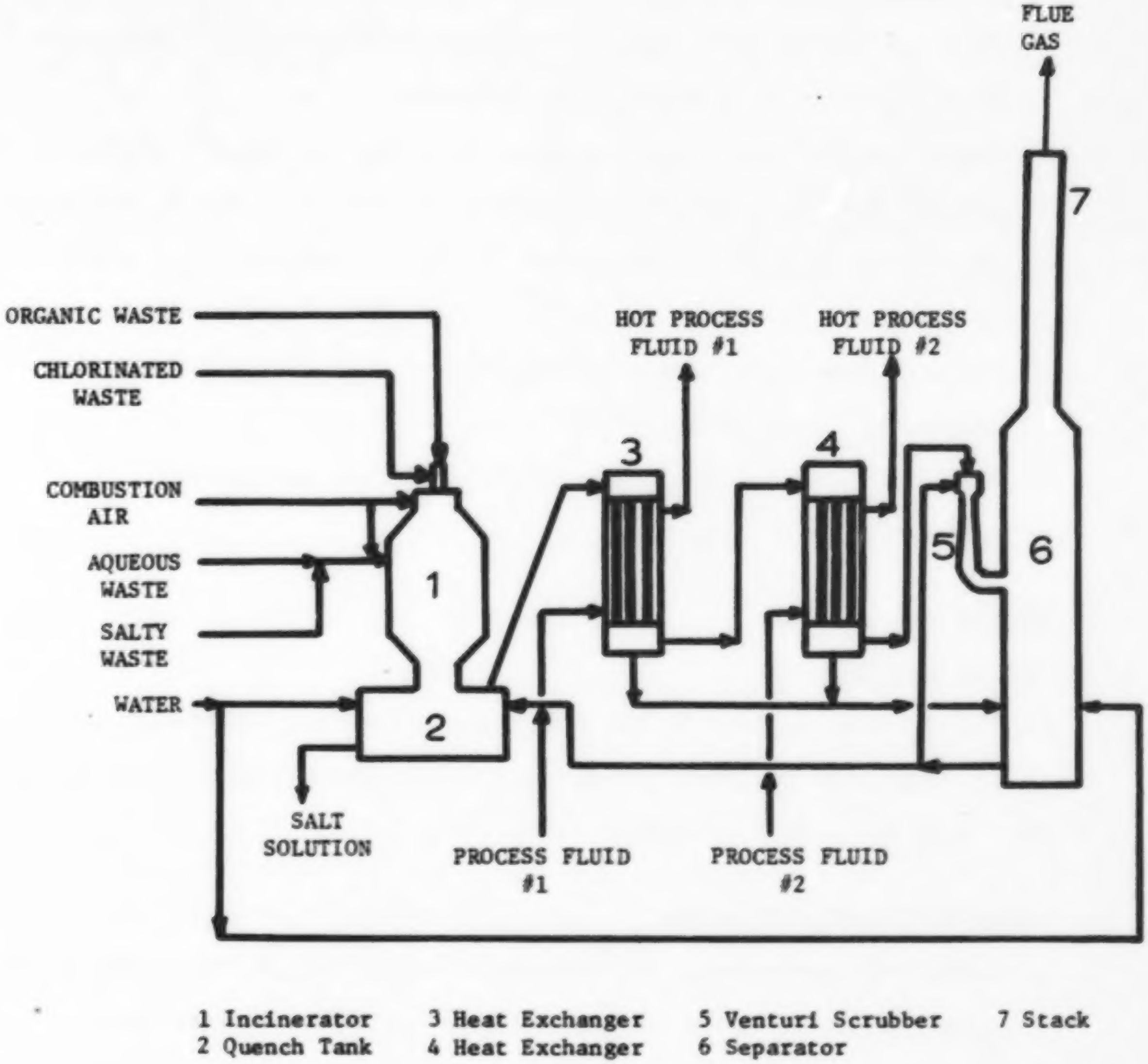

FLUE GAS
7
ORGANIC WASTE
CHLORINATED WASTE
COMBUSTION AIR
AQUEOUS WASTE
SALTY WASTE
WATER
HOT PROCESS FLUID #1
HOT PROCESS FLUID #2
3
4
5
6
1
2
SALT SOLUTION
PROCESS FLUID #1
PROCESS FLUID #2
1 Incinerator
2 Quench Tank
3 Heat Exchanger
4 Heat Exchanger
5 Venturi Scrubber
6 Separator
7 Stack

Figure 2. Integrated Waste Disposal System(5)

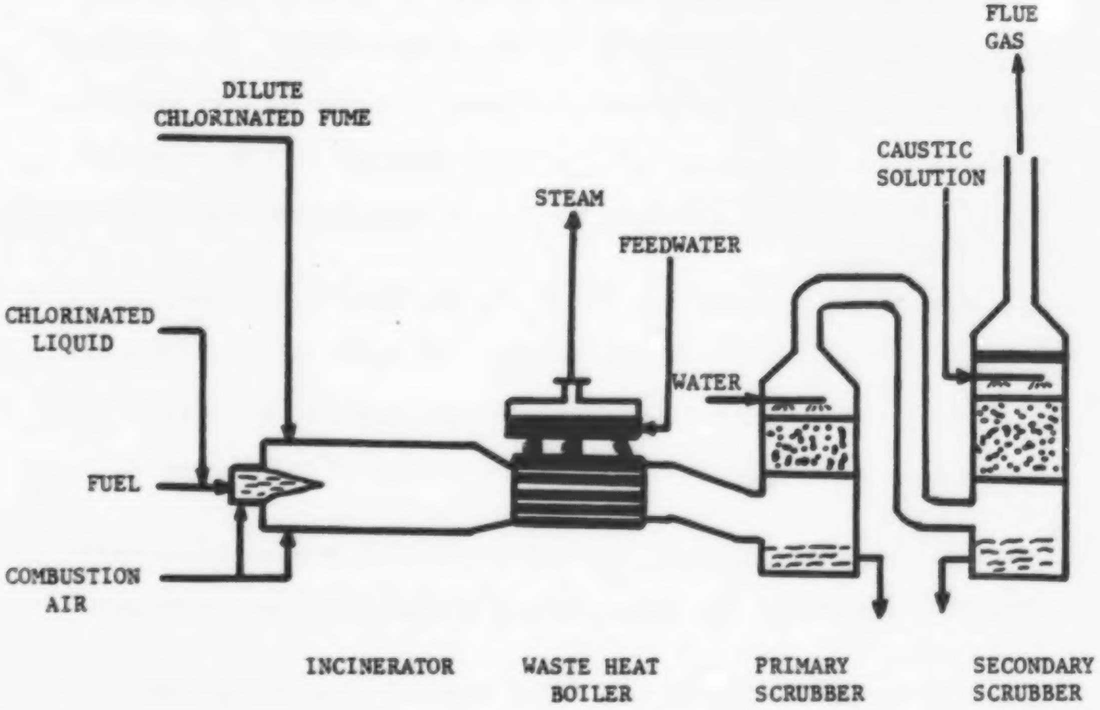

FLUE GAS
DILUTE CHLORINATED FUME
CAUSTIC SOLUTION
STEAM
FEEDWATER
CHLORINATED LIQUID
WATER
FUEL
COMBUSTION AIR
INCINERATOR
WASTE HEAT BOILER
PRIMARY SCRUBBER
SECONDARY SCRUBBER

Figure 3. Chlorinated Hydrocarbon Incineration System(4)

waste is also a proven technology.$^{(4-7)}$ Thus, no technology difficulty was encountered. The challenge to the process engineer is to achieve the reliability factor with lowest capital and operating costs. The system concept used here is the dual system approach. The primary system is the incineration-boiler-scrubber system, Figure 3, which is designed to handle the full load of the waste streams. The secondary system consists of only incinerator-scrubber system, and is used as back-up system in case of failure of the primary system. The secondary system should be large enough to handle the full load of both gaseous wastes and small enough so that the energy required to keep it ready is minimized. Liquid waste is used as fuel to keep the secondary system warm.

The system design concept for this system is that, in the event a problem developed in the primary system, the gaseous wastes will be automatically diverted into the secondary system. All the liquid wastes will then be stored in storage tanks until the primary system is back on stream.

D - Process Design Calculations. Material and energy balance calculations were then performed. The sizes of both systems were then identified.

Based on the above analysis, the other steps of front-end process engineering can then be performed.

EXAMPLE 3

Problem Definition

A chemical plant discharges an aqueous waste which consists of 5% hazardous organics and 95% water. An incineration system is required to dispose of the waste. The constraint of the application is that the total energy requirement must be minimized - by either reducing fuel requirement or generating steam as credits.

Front-End Process Engineering

A - Waste Characterization. The waste was analyzed and identified that, besides carbon, hydrogen and oxygen, the organics also contain sodium and phosphorus.

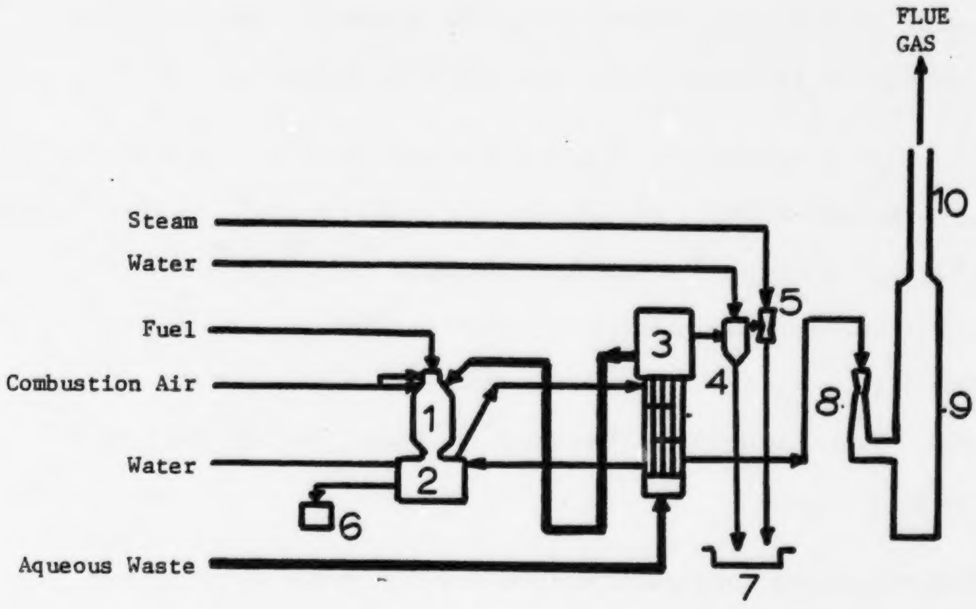
B - Process Requirement Definition. Pilot plant study is required to determine the time, temperature and excess air requirement for the disposal of the wastes in a specific type of incinerator design. Also, energy management is needed to minimize the total energy requirement.

C - Process Concept Development. To minimize energy requirement for alkali aqueous waste incineration, the system described in Figure 4 is the most efficient approach.(5) However, additional testing showed that the waste contained large quantity of volatile organics. The volatile compounds will contaminate the cooling water and require further treatment. Thus, the system illustrated in Figure 4 is not feasible for this application.

The applicable energy management systems for this waste are presented in Figure 5.(8) Process design calculation is then required.

D - Process Design Calculation. Material and energy balance calculations are performed on the four systems. The energy requirement for each system is presented in Table 2.

Based on the information obtained so far, further engineering and evaluation can then be performed to select the most practical and economical system.


FLUE GAS
Steam
Water
Fuel
Combustion Air
Water
Aqueous Waste
1
2
3
4
5
6
7
8
9
10

1 Incinerator
2 Quench Tank
3 Evaporator
4 Condenser
5 Steam Ejector
6 Salt Tank
7 Water
8 Venturi
9 Separator
10 Stack

Figure 4. Waste Heat Recovery for Alkali Waste Incineration(5)

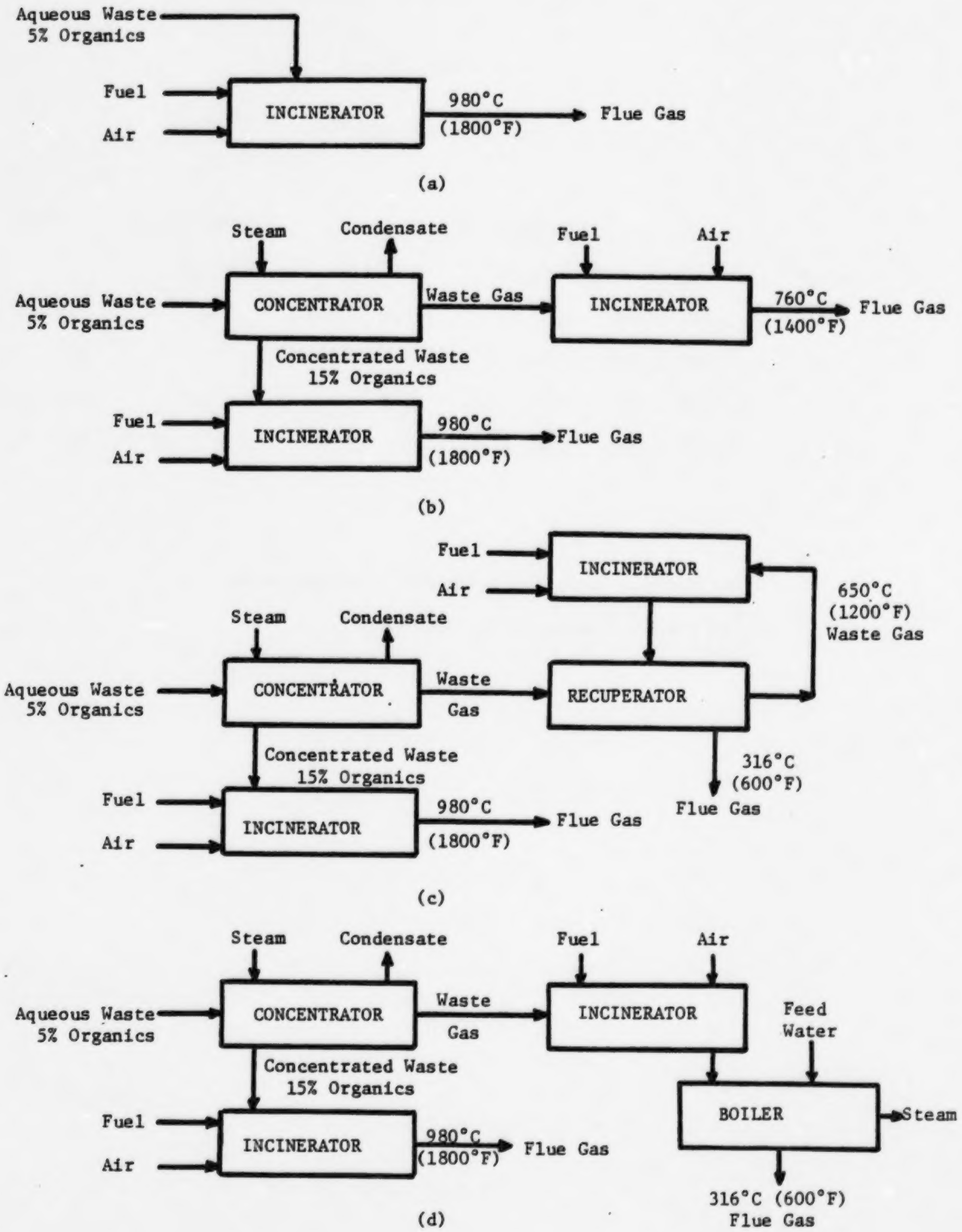

Aqueous Waste
5% Organics
Fuel
Air
INCINERATOR
980°C
(1800°F)
Flue Gas
(a)
Steam
Condensate
Fuel
Air
Aqueous Waste
5% Organics
CONCENTRATOR
Waste Gas
INCINERATOR
760°C
(1400°F)
Flue Gas
Concentrated Waste
15% Organics
Fuel
Air
INCINERATOR
980°C
(1800°F)
Flue Gas
(b)
Fuel
Air
INCINERATOR
650°C
(1200°F)
Waste Gas
Steam
Condensate
Aqueous Waste
5% Organics
CONCENTRATOR
Waste
Gas
RECUPERATOR
Concentrated Waste
15% Organics
316°C
(600°F)
Flue Gas
Fuel
Air
INCINERATOR
980°C
(1800°F)
Flue Gas
(c)
Steam
Condensate
Fuel
Air
Aqueous Waste
5% Organics
CONCENTRATOR
Waste
Gas
INCINERATOR
Feed
Water
Concentrated Waste
15% Organics
BOILER
Steam
Fuel
Air
INCINERATOR
980°C
(1800°F)
Flue Gas
316°C (600°F)
Flue Gas
(d)

Figure 5. Waste Heat Management Systems for Alkali Waste Incineration

Table 2

ENERGY MANAGEMENT(1)

	Energy Requirement			Energy Credit	Net
System(2)	Fuel	Steam	Total	Steam	
a	7326 (3150)	0	7326 (3150)	0	7326 (3150)
b	2070 (890)	1860 (800)	3930 (1690)	0	3930 (1690)
c	1489 (640)	1860 (800)	3349 (1440)	0	3349 (1440)
d	2070 (890)	1860 (800)	3930 (1690)	1023 (440)	2907 (1250)

1. Unit: KJ/Kg Aqueous Waste (Btu/lb. aqueous waste)
2. Systems are illustrated in Figure 5

EXAMPLE 4

Problem Definition

A speciality chemical manufacturer has an organic waste discharge from its reaction chamber. The waste contains not only hazardous organic compounds, but also hazardous metallic compound. The metallic compound is used as catalyst in the reactor and is very valuable. The objectives of the incineration system are to dispose of the organic waste safely, and to recover both waste heat and catalyst.

Front-End Process Engineering

A - Waste characterization. The composition of waste is available from the plant. The characteristics of the catalyst are also available.

B - Process Requirement Definition. The time, temperature, and excess air requirement must be determined by pilot plant testing. Pilot plant test is also necessary to evaluate the behavior of the catalyst at incineration temperature condition. Catalyst can be recovered in slurry form to be regenerated off-site. Steam is the preferred waste heat recovery means.

C - Process Concept Development. The basic system which can achieve all the objectives is illustrated in Figure 6. To ensure the success of the system, the behavior of the catalyst has to be studied. Test is necessary to determine the inter-reaction between the refractory material and the catalyst.

After study of the vapor pressure of the catalyst, it was found that the catalyst sublimed at very low temperature. Thus, the boiler can be designed without worrying about the molten or solid materials in the gas stream.

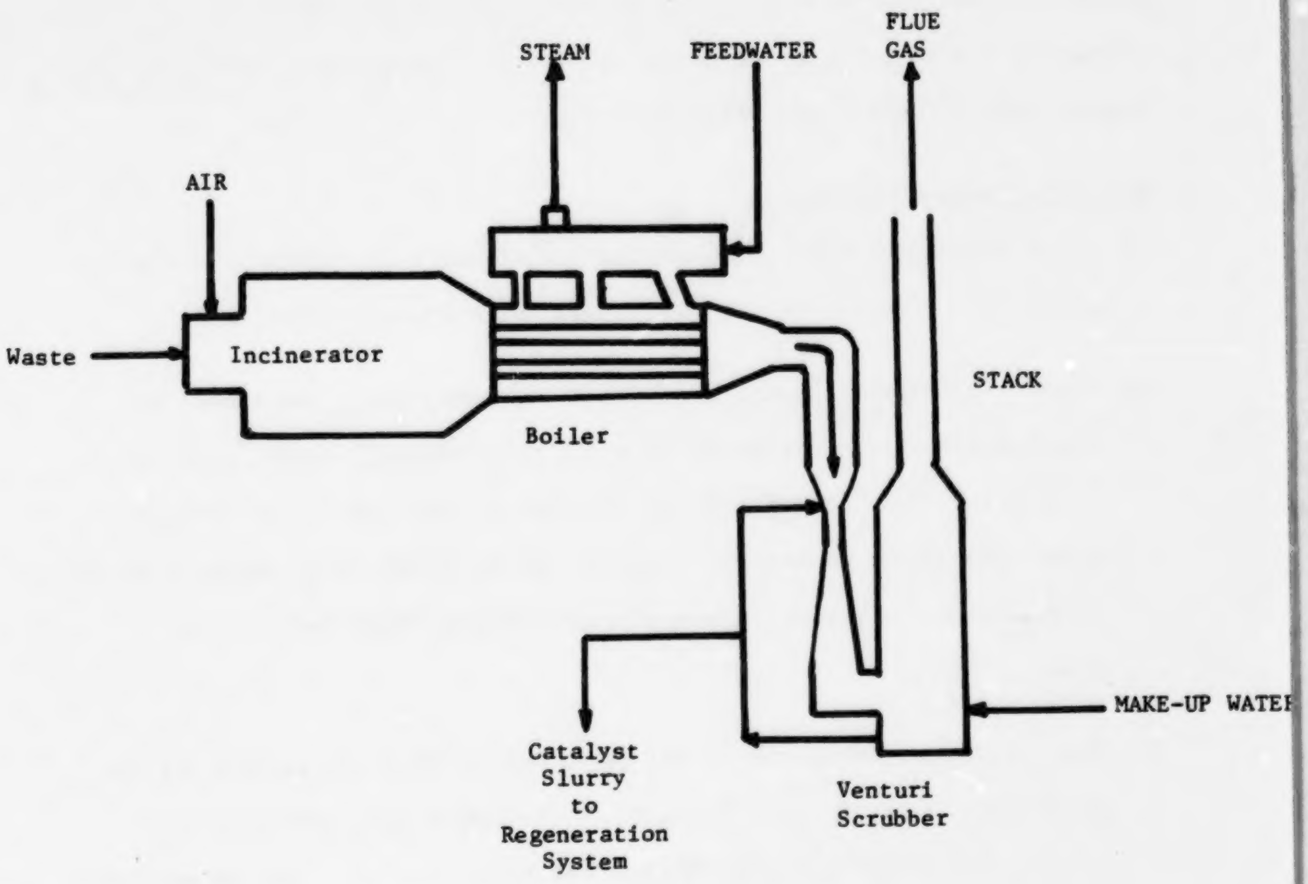

FLUE
GAS
STEAM
FEEDWATER
AIR
Waste
Incinerator
STACK
Boiler
MAKE-UP WATEF
Catalyst
Slurry
to
Regeneration
System
Venturi
Scrubber

Figure 6. Catalyst Recovery System

Since no technology difficulties were encountered, the system as illustrated in Figure 6 can then be engineered and developed.

SUMMARY

In this paper, the basic methodology for engineered system concept for hazardous waste incineration is presented. Examples were also used to illustrate the application of the methodology. From the examples, one can conclude that there is not a "step by step" rigid method for the engineered system concept. The concept is not a science, but an art. The process engineers not only have to understand all the scientific and engineering basis of incineration system design, but also have to be artists to make full use of their knowledge.

Another important feature of the engineered system concept is the dedicated incineration system concept. That is, design a waste incinerator for a process or a plant. The integration of incineration with process plant will solve the siting problems involved with commercial incineration system; will also offer the potential of reuse energy and byproducts in the process plant.

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THERMAL OXIDATION

V. C. MEUNIER
ABCO Industries, Inc.
Roebuck, SC

ABSTRACT

Thermal oxidation combines the processes of pyrolysis and oxidation. Thermal oxidation is generally associated with the complete destruction of organic compounds comprising fossil fuels and organic wastes. In this paper, emphasis will be applied to the destruction of liquid or pumpable organic chemical wastes.